Chapter I

INTRODUCTION

1.1 Metallochromic Reagent

1.1.1 Metal indicator

Metal indicators are substances that undergo a marked color change when the concentration of free metal ion in a solution changes. These indicators usually have properties typical of acid-base indicators. The anion of the indicator is a base capable of donating one or more electron pairs and can hence function as a ligand. This base can react with a hydrogen ion or a metal ion (or with other electrophilic species). Often the color of the metal complex is about the same as that of the free indicator anion, and the color change occurs when one or more hydrogen ions are replaced by a metal ion. It is possible to classify the metal indicators broadly according to their mode or mechanism of reaction into five types.

1.1.1.1 Metallochromic indicators. Metallochromic indicators are substances which react with metal ions to form colored products having the properties necessary in visual indicators. The color-species is usually due to the formation of a chelate complex, but there are a few instances where inorganic anions such as iodide or thiocyanate form simple co-ordination

complexes of sufficient absorption in the visible range of the spectrum. Metallochromic indicators can be classified on the basis of their structures to be: azo dyes, phthaleins, sulfophthaleins, triphenylmethane dyes, anthraquinone dyes, and phenolic substances.

1.1.1.2 Fluorescene indicators. Fluorescene indicators have also been called " metalfluorechromic indicators " (1) or " metalfluorescent indicators " (2). These are similar to metallochromic indicators in their chelation properties and mechanism of reaction except these substances may exhibit fluorescence rather than absorption changes. On formation of a chelate the fluorescence of the free form of the indicator is quenched or the chelate itself exhibits fluorescence. Chelometric titrations with these indicators are usually performed with the solution subjected to ultraviolet illumination.

1.1.1.3 Redox indicators. If a solution containing a metal in two different oxidation states in reversible equilibrium is titrated with a complexing agent, a sudden change in redox potential occurs at the end-point owing to the difference in the stabilities of the complexes of the metal in its two oxidation

states. The jump in redox potential can be detected potentiometrically or with a color indicator. As the method can be applied only to special systems and as many of the indicators react slowly, the method has its limitations.

1.1.1.4 <u>Diverse metal-sensitive and metal-specific indicators</u>. A further group of metal indicators, which are themselves colorless. So the detection of the end-point is based on somewhat different principles. The color formation is attributed in some cases to charge transfer spectra or to alteration of the ligand field strength. The color of the uncomplexed indicator does not interfere, and hence, if necessary, a fairy high indicator concentration can be used. For most colorless indicators, which as a rule are less sensitive than the indicator dyes, this visually detectable color intensity corresponds to a molarity between 10^{-4} and 10^{-6} (3). In selected cases, the action and sensitivity of such indicators may be improved by the addition of an organic solvent, such as alcohol or a ketone, to the titration medium.

1.1.1.5 <u>Turbidity indicators</u>. The end point of a complexometric titration can be detected by observing

the appearance of a precipitate. Well known is the classical method of Liebig-Denigès (4): a solution of a cyanide is titrated with silver nitrate until a precipitate of silver argentocyanide is formed. Turbidity indicators are of little contemporary interest for chelometric titration.

1.1.2 Metallochromic indicators

Körbl and Přibil (5) introduced the term metallochromic indicator to designate a metal indicator that was acid-base activity and that functions in a chelometric titration by reacting with the metal ion to form a chelate substantially soluble in the titration medium. In the structure of such indicators one or more ligand groups must be joined directly to a resonance system. (Such indicators are usually so-called mordant or chrome dyes). The change in the spacing of low-lying π electron energy levels resulting from the chelation causes a shift in the wavelength of the absorption bands and hence a change in color. The extent of the shift may depend to some extent on the metal ion involved. For this reason, metallochromic indicators are applicable to various metal ions. Since most metallochromic indicators function in this way as acid

base indicators,pH has a profound effect on their mode
of action and range of application. Sharper end points
are usually obtained when an extremely small concen-
tration of a metallochromic indicator is employed in
a chelometric titration. For this reason the indicator
in either its metallized or its free form need only be
added in concentration of $10^{-6} - 10^{-5}$ M.(6) to give a
color change that is still clearly detectable. The
indicators are arranged principally according to their
structures. Napthylazo compounds constitute a large
group, most of which have hydroxyl groups substituted
adjacent to the azo bond, while a few also depend on
carboxyl or arsonic acid groups. These azometallochromes
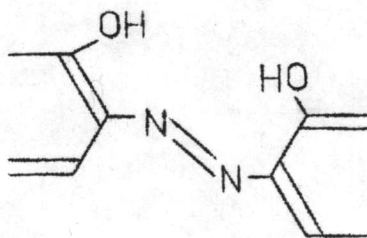
depend on reaction with the azo bond as well as with
the hydroxyl group.

The second group comprises phenolic compounds
ranging in complexity from catechol to hydroxy-substituted
triphenylmethane compounds. All these molecules depend

solely on the presence of vicinal hydroxyl groups for their activity. This differentiates them from the hydroxylazo indicators of the first group and those described below.
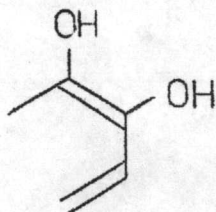
The third group also depends on the presence of a hydroxyl group for its metallochromic response, but the principal reactive center in the molecule is an " ortho " substituted aminomethyldicarboxymethyl group. Attachment of a metal ion at this center in the molecule results in reaction with the adjacent phenolic group with consequent changes in the chromophore of the organic reagent.
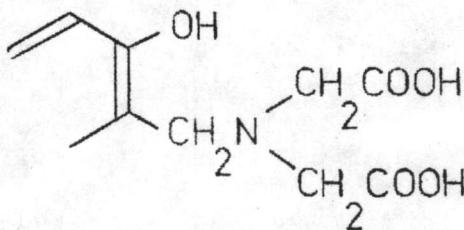
The forth group deals with indicator substances not catered for in the above sub-classification of

direct metallochromic indicators.

1.2 Beryllium

1.2.1 History

Beryllium was discovered in 1797 by Louis Nicholas
Vauquelin (9). He noted the formation of a precipitate
as the result of boiling a solution of beryl in potassium
hydroxide. Thus, beryllium was first isolated as the
hydroxide. In 1828 both Wöhler (10) and Bussy (11)
independently isolated the metal by reducing the chloride
with potassium in a platinum crucible. Wöhler named the
element beryllium, symbol Be, while Bussy used glucinium, Gl;
the double nomenclature persisted until quite recently,
but glucinium has now been completely superseded by
beryllium.

1.2.2 Occurrences

The beryllium content of the earth's surface rocks
has been estimated at 4 - 6 ppm. (12). The most important
beryllium mineral is beryl, beryllium aluminium silicate
($3BeO.Al_2O_3.6SiO_2$), which contains approximately 3.4
to 5.0 % beryllium. This principal ore occurs as a
minor constituent of pegmatitic deposits and is mined
primarily as a by - product of other minerals present in

such deposits, such as feldspar, spodumene, and mica. approximately sixty beryllium – containing minerals have been identified, for example; phenacite (Be_2SiO_4), contains 16.4 % beryllium, helvite $[3(Mn,Fe)BeSiO_4 \cdot MnS]$, a complex beryllium sulfosilicate, contains 4.0 % beryllium, bertrandite $[Be_2(BeOH)_2Si_2O_7]$, contains 0.5 % as beryllium oxide.

1.2.3 <u>Chemical properties</u>

Beryllium, with atomic number 4, belongs to the alkaline group of metals in the periodic table. The atomic weight on the chemical scale is 9.013 $\pm$ 0.0004. The electronic configuration is $[He]2S^2$. The only valence it exhibits is 2. Beryllium has the least in common with the other elements of its group and it shows diagonal relationship similarities with aluminium in group III. Beryllium differs from the rest of the group partly because it is extremely small and partly because of its comparatively high electronegativity. Beryllium atom has a metallic radius of 0.89 A. The smaller size increases the effect of the nuclear charge. Its ionization potential is much higher than the other members, which makes beryllium far less electropositive in all its chemical behavior than the rest of the group.

Thus when beryllium reacts with another atom, the

difference in electronegativity is seldom large and ber-
yllium is predominantly 2-covalent in its compounds. Its
salts are extensively hydrolyzed and therefore, solutions
of all beryllium salts are acid. Beryllium is, however
readily attacked by all of the commonly used acids, strong
or diluted, except nitric acid, which if cold and concen-
trated, has little effect. In concentrated acid solutions
beryllium appears to exist as $\left[Be(H_2O)_4 \right]^{2+}$ ions, and
these occur in several salts. But they never have more
than 4 molecules of water of crystallization. The water
in such salts is rather firmly bound ; $\left[Be(H_2O)_4 \right]Cl_2$,
for example, loses no water over P_2O_5.

In general, complex formation is favored by small
highly charged ions with suitable empty orbitals of
approximately the right energy. Thus beryllium forms
many complexes. In most cases beryllium is four-coordi-
nate in complexes and the tetrahedral arrangement adopted
correlates with the orbitals available for complex for-
mation.

1.3 Spectrophotometric Determination of Beryllium

Table I shows various metallochromic reagents, opti-
mal conditions and information of spectrophotometric
methods of analysis for beryllium.

Table I Metallochromic reagents for beryllium from the year 1966-1972

Reagents	Stoich.	pH	λ max (nm)	ε	Adherence to Beer's law	Conditions of interfering ions	Ref.
1966							
<u>Orthohydroxyazo compound</u>							
Arsenazo I	ML_2 ML	12.2 5.0	580	1×10^4	0-0.6ppmBe		18
Beryllon IV		5.0-7.0	530			the foreign ions could be masked by complexon	19
Chlorophosnazo P.		9.4	520			no interference arised from the presence of 100_γFe; 200_γMn or Cu: 300_γAl,Ca or Mg; 500_γMo; 1000_γNi; or Co; 25_γSi or 200_γTi	20
Eriochrome Blue SE		6.2-6.8	610	1.1×10^4	0.02-0.3ppm Be	Be can be found in the presence of 50_γFe(II, III),Mn(II),Ca andMg. Cu(II),Al,Zn,Co,Ni interfere	21

Table I Continued

Reagents	Stoich.	pH	λ max (nm)	ε	Adherence to Beer's law	Conditions of interfering ions	Ref.
1967							
Orthohydroxyazo compound							
Pontacyl Violet 4BSN		6.5-7.4	620	2.46×10^4	<0.3ppm Be	Al,Fe(III),Cu(II),Sc Cr(III),PO_4^{3-}interfere	22
Nonazo compound							
5-Hydroxychromone		7.0-7.5	398			Al^{3+},Pd^{2+},Fe^{3+},$Cu^{2+}$and Ti^{4+}give a positive error but In^{3+},Tl^{3+}, $PO_4^{3-}$and F^-give a negative error	23
Aluminon		4.8	530		10-40ppm Be	F^-interfere for all concentration	24
1968							
Orthohydroxyazo compound							
Azo Fuchsine GN		9.0	550			Cu,Fe,Mn,Zn,Al,Mg, interfere	25

Table I Continued

Reagents	Stoich	pH	λ max (nm)	ε	Adherence to Beer's law	Conditions of interfering ions	Ref.
Picraminazochrome	ML	5.5	635			$Cu,Fe^{3+},Zr,Ca,Ba,Sr,Zn,$ Ga andSn interfere.Al interfere seriously be-cause the reagent is highly sensitive for Al	26
N-methylanabasine-(α'-azo-6)-m-amino phenol	ML_2	1.8-3.0	530		$0.1-0.8 \gamma Be/ml$	The following elements and substances(the ratio of element to Be was in-dicated in parenthesis) did not interfere with Be determination:Mn(400) Cd(200),Ge(100),Mg(90), Ca(50),Zn(25),Cr(19), Al(9),and Th(4);complex-onIII(150),tartrate and oxalate(30),citrate(25) F^-interfere.The inter-fering effect of Ni(650), $UO_2^{2+}(480),Co(250),Cu(150)$ Nb(25),$Fe^{2+}$and Zn(20), V(12),Ti(10),Ta(5)were	27

Table I Continued

Reagents	Stoich.	pH	λ max (nm)	ε	Adherence to Beer's law	Conditions of interfering ions	Ref.
						masked by complexonIII	
Azo compound							
p-Sulfophenylazo-salicylic acid	ML	11.7	450	1.2×10^4		Cu had to be separated by electrolysis, Al(III) Fe(III) could be masked with complexonIII	28
Nonazo compound							
1-Hydroxyxanthone	ML		420	3291			29
1969 Orthohydroxyazo compound							
Beryllon II		10.0-11.0	525	2.0×10^4	0-15 γBe/50ml	For the determination of 5 γBe, the following were tolerable: 40mgZn, 10mg. Al, 8mg. Cu	30

Table I Continued

Reagents	Stoich.	pH	λ max (nm)	ε	Adherence to Beer's law	Conditions of interfering ions	Ref.
Nonazo compound							
Trilon B		12.3-12.4	625		0.03-0.13μgBe per ml.	50-300γFe,Cu,Si,Al,Ca, Mg,Ni,Co,Mo,and Mn did not interfere with the determination of 0.05-2.0γBe	31
Chrome Azurol S		5.1	610	9.9×10^4	0.1-3γBe/25ml.	F⁻(5γ),Cu(1mg.), Al(100γ),V(V)(100mg) interfere.Cu and Al were masked with 1 ml. of 0.1% Na_2HPO_4 solution and V(V) was removed by filtration of the precipitate of Zephiramine vanadate	32
Chrome Azurol S in the presence of polyvinyl alcohol	M_2L_2	6.5±0.4	615	52,000	5-130ng.Be/ml.	thediverse ions could be removed by Ca-EDTA chelate	33

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Table I Continued

Reagents	Stoich.	pH	λ max (nm)	ε	Adherence to Beer's law	Conditions of interfering ions	Ref.
Eriochrome Cyanine R.		6.7-7.2	595		0.018-0.055 ppmBe	$Cu^{2+}, Al^{3+}, Fe^{3+}, Cr^{3+}, Zr^{4+}$ and U^{6+} interfere	34
Ruffigallol		7.0	540		2-10 γ Be/ml	Al,Th,Zr,Hf interfere seriously. $Bi^{3+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Ga^{3+}, In^{3+}, Fe^{3+}, Pb^{2+}, Pb^{4+}, Mn^{2+}, Mo^{6+}, Ni^{2+}, Se^{4+}, Tl^{3+}, Ti^{4+}, U^{6+}, V^{5+}$, to a lesser content. All were removed by extraction of their quinolates with $CHCl_3$	35
1970 Nonazo compound							
Phenoxydinaptho-fuchsonedicarboxylic acid	ML	5.0-8.0 11.5-13.0	630 540			in neutral medium large amount of Cs,Na,K,Li, Ba,Ca,Ag,Fe(I),Cu(I), Pb(II),and Sr(II),did not interfere.Cu(II), Cr(III)5µg/ml;Ti(IV),	36

Table I Continued

Reagents	Stoich.	pH	λ max (nm)	ε	Adherence to Beer's law	Conditions of interfering ions	Ref.
						Al(III),Fe(III),Ga(III) Zn(II),Cd(II),Co(II), and Ni(II) did.	
Eriochrome Brilliant Violet B	ML_2	5.8-7.0	560	5.95×10^4	0.02-0.15ppm Be	Cu(II),Cd,Ni,Al,Fe(III) Cr(III),Y,and the rare earth elements interfere seriously	37
Chromal Blue G	ML_2	6.0	610	3.1×10^4	<0.3ppmBe	Cu,Al,Fe(III),Ni,Sc,Y, rare earth elements interfere seriously, SO_4^{2-},Cl^-,NO_3^-,OAC^-,did not interfere.$C_2O_4^{2-}$ F^-,citrate,PO_4^{3-}, EDTA bleach the complex	38
Chrome Azurol S		5.1	610		0.05-2 γBe	Al $\leqslant$14mg.did not interfere	39
Methyl Thymol Blue		5.0	500	1.32×10^4	0.04-0.36ppm Be	Addition of a small amount of EDTA was effective in masking the diverse bivalent ions.	40

Table I   Continued

Reagents	Stoich.	pH	λ max (nm)	$\mathcal{E}$	Adherence to Beer's law	Conditions of interfering ions	Ref.
Solochrome Azurine BS	ML	4.0–5.5	560	4.5×10^3	$\leqslant 3.0$ ppmBe	$Ca^{2+}, VO_2^{2+}, UO_2^{2+}, Al^{3+}, Zr^{4+}$ $Ce^{4+}, S^{2-}, SO_3^{2-}, C_2O_4^{2-}, PO_4^{3-}$ and AsO_4^{3-}, interfere seriously; $Na^+, K^+, Rb^+, Cs^+,$ $Tl^+, Ba^{2+}, Mg^{2+}, Sr^{2+}, Cd^{2+},$ $Pb^{2+}, Sn^{2+}, Cu^{2+}, Mn^{2+}, Zn^{2+}$ $Hg^{2+}, Ni^{2+}, Cr^{3+}, Sb^{3+}, La^{3+}$ $Ce^{3+}, Cl^-, Br^-, I^-, CN^-, NO_2^-$ $NO_3^-, OAc^-, BO_3^{3-}, SO_4^{2-}$ did not interfere.	41
1971 **Orthohydroxyazo compound** Arsenazo III	M_2L	5.0–6.5	580	1.8×10^4		The method might be used for solution containing 0–10μgBe/25ml. and 100–500fold excesses of Cu,Mg,Zn,Cd,Mn,Pb,W, Mo,Ce(III),La,Th,Sb,Tl(I) $OAc^-, C_2O_4^{2-}$,citric acid.	42

Table I Continued

Reagents	Stoich	pH	λ max (nm)	ε	Adherence to Beer's law	Conditions of interfering ions	Ref.
Thorin	ML_2	10.4	523	1.36×10^4	0.1-1.0μmol Be/25ml.	The method is highly selective if EDTA was added (Ca,Mg,Co,Cr,Cu, Fe,Mn,Ni,Th,Zr,inter-fere.Anions did not.	43
Nonazo compound							
Eriochrome Cyanine R	$M_2L_2^4$	7.0	522		0.01-0.3μg Be/ml	diverse ions were masked by EDTA and Ca was added to reduce the EDTA com-plexation of Be.	44
Chrome Azurol S with Zephiramine		5.2	610	1.09×10^5	$4 \times 10^{-3}-$ 8×10^{-2} ppmBe		45
Chrome Azurol S with cetyltrime-thylammoniumchlo-ride	ML_2		619	0.91×10^5	$6 \times 10^{-7}-$ 6×10^{-6}M.Be	Al,Th,U,Fe,Cu,V,Ti,Au, Zr,Sn,interfere	46
Methylthymol Blue			510			$C_2O_4^{2-}$,citrate,tartrate $F^- >$ 0.002M.nitrilotri-acetic acid;5 fold	47

Table I Continued

Reagents	Stoich.	pH	λ max (nm)	ε	Adherence to Beer's law	Conditions of interfering ions	Ref.
						amount of Al,Fe^{3+},Ti^{4+} interfere	
1972							
Orthohydroxyazo compound							
Monosalicylazochromotropic acid	ML	12.0	595		0.16–4.0µgBe per ml.	Cu,Al,Ni,and Co could be partly masked with complexonIII	48
Nonazo compound							
2'-Hydroxychalcone	ML_2	5.5–6.2	460		0.5–6.0ppmBe	$C_2O_4^{2-}$,F^-,tartrate,citrate interfere.Tolerance limits were Cr(III)50,Fe(III) 100µg;VO_3^-1.5,Al2,UO_2^{2+}3, and Th(IV) 10 mg for the determination of 0.1 mg.Be/25 ml.	49
Methylthymol Blue	ML	5.0	500	1.325×10^4	$\leqslant 9.0$ µgBe		50

Table I Continued

Reagents	Stoich.	pH	λ max (nm)	ε	Adherence to Beer's law	Conditions of interfering ions	Ref.
Methylthymol Blue	ML	5.8	490	8.7×10^3	2.3×10^{-6}– 1.1×10^{-4}M.	diverse ions were eliminated by masking	51
Glycinethymol Blue		10.0	453		0.5–20µgBe/50ml.		52
Cyclopentanone-2-carboxanilide		7.0–10.5	332	9900		Ag(I),Tl(I),Cd(II),Cu(II) Co(II),Pb(II),Zn(II),Bi (III),Al(III),Ga(III), In(III),Cr(III),Fe(III), Ce(III),Th(IV),V(IV), Mo(IV),U(VI),W(VI),Zr(IV) Ti(IV) could be masked by EDTA	53

1.4 Reason for Undertaking this Problem

Nowadays beryllium has increased its potential uses in many field. But it is still a problem metal, however, rare in occurrence, difficult and costly to extract.

Many organic dyes have been tried as a metallochromic reagent for the determination of beryllium by spectrophotometric method. From Table I, which shows the previous studies of the subject, it is seen that, the reagents used can simply divided into two groups; azo and non azo compounds. The molar absorptivities of the latter are higher than the former. And amongst the azo compounds, the orthohydroxyazo group is widely used.

The purpose of the present investigation is therefore to synthesize a new orthohydroxyazo dye and use it as a new reagent for the determination of trace amounts of beryllium, and try to achieve the optimal conditions. Study of the diverse ions is next to consider. It is hoped that EDTA may be used as a mass masking agent for the foreign ions in order to increase the selectivity of the method.