CHAPTER I

INTRODUCTION

1.1 Metal Indicator

A metal indicator(1) is an indicator which exhibits one visual response in the presence of a metal ion through complexation with it and a different one in its absence. Metal indicator mostly has an azoic structure and diverse structure. Generally they are widely used in chelometric titrations for the end-point detection.

During the major portion of a direct chelometric titration, the metal indicator exists almost entirely in its "metallized" form and the "free" metal ion in progressively chelated by the chelon titrant. At the equivalence point, the chelon removes the traces of the metal from the metal-indicator complex and the indicator changes to its "free" form, thus signaling the end point. It is possible to classify the metal indicators broadly into four types according to their mode or mechanism of reaction.

1. Metallofluorescent indicators. (Metalfluorochromic indicators)

The chelation properties and mechanism of these indicators are similar to metallochromic indicators except that 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 such indicators are usually performed with the solution subjected to ultraviolet illumination.

2. Diverse metal-sensitive and metal-specific indicators.

This group of metal indicators are simple inorganic or organic substances, and which in general are themselves colorless, function to form colored complexes with a select number of metal ions. The color formation is attributed in some cases to charge-transfer spectra or to alteration of the ligand field strength. Such indicators usually exhibit for lower molar absorptivities, and hence are less sensitive than metallochromic indicators. In selected cases, the action and sensitivity of such indicators may be improved by the addition of an organic solvent, such as an alcohol or a ketone, to the titration medium. Common examples of such metal-sensitive indicators include thiocyanate ion, thiourea, iodide ion, salicylic acid, sulfosalicylic acid, and Tiron.

3. Turbidity indicators.

These indicators form finely divided insoluble substances with the metal ion. Thus, oxalate ion has been employed in the titration of EDTA with calcium ion, the end-point is signaled by the formation of insoluble calcium oxalate. Turbidity indicators are of little contemporary interest for complexometric titrations.

4 Metallochromic indicators.

Körbl and Přibil introduced the term metallochromic indicator(1) to designate a metal indicator that has 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 directly jointed to a resonance system (such indicators are usually socalled mordant or chrome dyes). The change in the spacing of low-lying π-electron energy level resulting from the chelating causes a shift in the wavelength of the absorption bands, and hence a change in colour. The extent of the shift may depend to some extent on the metal ion involved, but the extent of the shift is a general property. For this reason, metallochromic indicators are applicable to a variety of metal ions, their use being limited usually by other factors, such as the formation of complexs with certain ions which are either too weak or too strong or which are too slow to substitution ability to permit their use in the direct chelometric titration of such ions.

Metallochromic indicators usually show significant acid-base indicator activity associated with the dissociation of protons of groups linked to the resonance system (or their protonation). The colour changes exhibited upon chelation usually fall within the ranges that can be elicited by pH changes, since the electronic configuration of the resonance system is similarly influenced by dissociation of protons (or protonation) and by chelation. The existence of such acid-base indicator activity often limits the usefulness of a metallochromic indicator to a definite (and frequently restricted) pH range.

Sharper end points are usually obtained when an extremely small concentration of a metallochromic indicator is employed in a chelometric titration. For this reason the indicator in either its metallized or its free from should have a large molar absorptivity in the visual spectral region, making possible its use at concentrations in the order of 10^{-5} molar.

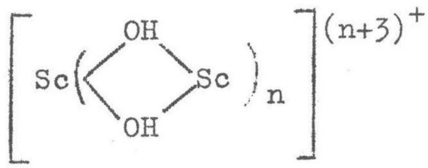
1.2 Scandium

Scandium was discovered in 1879 by L.F Nilson (2) and is found in a few rare minerals such as wolframite, wiikite and euxenite to the extent of 1 % or 2 % Sc_2O_3. Scandium has an electron configuration (3) $[Ar]3d^1 4s^2$, which is a congener of aluminium, but is decidedly more basic in its properties, it is in many respects quite similar to yttrium and the lanthanides. It is not a rare element, being as common as arsenic and twice as abundant as boron, but its chemistry is not on the whole well known. This is due partly to the absence of rich sources of the element and also to the difficulty of obtaining it in a pure state.

Scandium metal is obtained by the electrolysis of fused scandium chloride. It is dimorphic and crystallises with the close - packed hexagonal structure or the close - packed cubic structure. It is easily oxidised. When heated in nitrogen it yields the interstitial nitride ScN, which is decomposed by water with the liberation of ammonia.

Scandium has only the III oxidation state in which it gives the oxide (Sc_2O_3), halide (ScX_3) and oxohalide (ScOX) as well as numerous salts of oxo acids. The possibility of being a dipositive oxidation state has been rather carefully examined and there is no evidence for its existance.

The scandium ion, being smaller, has a much greater tendency to hydrolysis than the lanthanide ions, and polymeric species as indicated below have been shown to arise with



chain length increasing as pH increases. It is perhaps to be expected that, since it is closely related to both aluminium and the elements of the first transition series, scandium ion forms complexes for more readily than do the lanthanides. For this reason, the methods of determination of scandium are based on complex formation with the cooperation of spectrophotometric studies.

1.3 <u>Metallochromic Indicator</u> (or Metallochrome) for Scandium.

Many organic compounds had been used as metallochromic reagents for scandium. The works which had been done were summarized in Table I.

Table I

Metallochromic Indicators for Scandium.

No	Reagents	pH	λ_{max} (nm)	Stoich	ε	interfering ion	ref.
1	Pontacyl Violet 4 BSN	6.4-7.2	630	-	$1.37x10^4$	Al,Fe,Cu,Ni,Cr,Be,PO_4^{-3}	4
2	Chrome Azurol S.	5.6	550	ML_2	$2.70x10^4$	F^-,PO_4^{-3},$C_2O_4^{-2}$,tartrate,citrate	5
3	Lumogallion	-	530	ML	$1.02x10^4$	EDTA,Al(III),Be(II),U(VI), Fe(II),Th(IV),Cu(II),Y(III)	6
		-	500	ML	$1.40x10^3$	Zr(IV),W(VI),> 100fold of Zn(II) Pb(II),Sn(II)	
4	Naphthyl Azoxine	4.5	420	-	$8.00x10^3$	Cd(II),Bi(III),> 50fold of Mn(II),Tl(III),>10 fold of PO_4^{-3}, >5 fold of Al(III),Zr(IV),>0.5 fold of Th(IV),Fe(III),Cu(II), most metal,PO_4^{-3},$C_2O_4^{-2}$,tartrate	7
5	N,N'-bis(2-hydroxy-5-sulphophenyl-C-cyano) formazan	5.2	590	ML	$1.30x10^4$	———	8

Table I (continued)

No	Reagents	pH	λ_{max} (nm.)	Stoich	ε	interfering ion	ref.
6	Magnezon	5.0-5.5	570	-	1.10×10^{4}	———	9
7	3,4',5,7-tetrahydroxy-flavone(kaempherol)	3.0	415	ML	8.41×10^{3}	UO_2^{+2}, Th^{+4}, Mo^{+6}, Fe^{+3}, Ti^{+4}, Zr^{+4}, Be^{+2}, Al^{+3}, Ni^{+2}, Co^{+2}, V^{+5}, PO_4^{-3}, SO_4^{-2}, $C_2O_4^{-2}$ tartrate, citrate	10
8	Chrome Azurol S.	5.5	625	-	1.37×10^{5}	Al^{+3}, Ga^{+3}, In^{+3}, PO_4^{-3}, F^-	11
	and Zephizamines	5.0	560	-	-	———	12
9	Glycinecresol red	5.2	490	ML_3	2.1×10^{4}	Hf, In, Ga, Tl, Fe, Cu, Al, V, oxalate, citrate, F^-, Complexon(III), PO_4^{-3}	13
10	Stilbazochrome II	1.5-2.5	680	ML	2.35×10^{4}	———	14
11	Methylthymol blue	3.1	582	ML_2	-	———	15
12	Pyrocatechol violet	6.0	-	ML	1.87×10^{4}	———	16
13	Chromal blue G.	6.0	590	ML_2	3.14×10^{4}	———	17
14	1,5-bis(2-hydroxy-3,5,6-trichlorophenyl)-3-acetyl-formazan	4.7-6.5	675	ML_2	2.70×10^{4}	Cu(II), Co(III), Fe(III), Ga, In, Pb(II), Hg(II), V(V), F^-, SO_4^{-2}, PO_4^{-3}	18

Table I (continued)

No	Reagents	pH	λ_{max} (nm.)	Stoich.	ε	interfering ion	ref.
15	Bromocresol green	4.0-4.6	520	ML	$6.00x10^3$	———	19
	Bromocresol purple	4.0-4.2	470	ML	$8.15x10^3$	———	
	Bromocresol blue	4.0-4.2	480	ML	$1.40x10^3$	———	
16	Eriochrome brillion violet B.	-	562	ML_2	$6.40x10^4$	$C_2O_4^{-2}$, F^-, citrate, EDTA	20
17	Eriochrome Azurol G.	6	610	ML_2	-	Se, Be, Cu(II), Al, Fe(III), Y, Th, rare earth, $C_2O_4^{-2}$, F^-, citrate, EDTA	21
18	1,5-diantipyrinyl-3-cyano formazan	4.5 0.3	552	-	$6.00x10^4$	———	22
19	4-(2-thiazolylazo) resorcinol	8.1	540	ML_3	$5.06x10^4$	BO_3^-, tartrate, PO_4^{-3}	23
20	Phatalexon S.	1.3-6.0	530	ML	$2.48x10^4$	Mn^{+2}, Co, Ni, Ge, Pb, Cu, UO_2^{+2}, Th, Ti, Zr, Hf, Ga, In, Fe^{+3}, Al, F^-, PO_4^{-3}, $C_2O_4^{-2}$ and SO_4^{-2}	24

Table I (continued)

No	Reagents	pH	λ_{max} (nm.)	Stoich	ε	interfering ion	ref.
21	Thymolphathalexon S.	2.3-3.8	-	M_2L	2.6×10^{4}	Th, Hf, Zr, Ti, Ga, Al and Fe^{+3}	25
22	Xylenol orange	2.5	556	ML	2.39×10^{4}	——	26
	Methylthymol blue	3.0	580	ML	1.23×10^{4}	——	
	Pyrocatechol violet	5.5	-	-	-	——	
	Chromazurol S.	4.0	580	ML	1.23×10^{4}	——	
		6.5	560	ML_2	2.35×10^{4}	——	
	Glycinecresol red	5.1	490	ML_2	2.1[illegible]$\times10^{4}$		

1.4 Reasons for Undertaking this Problem

It appears that the reagents used for the determination of scandium spectrophotometrically as recorded in Table I may be classified into two main groups namely azo compounds and non-azo compounds.

From Table I, the reagents in the azo group are Pontacyl violet 4 BSN, Naphthyl azoxime, N,N'-bis (2- hydroxy-5-sulphonyl-C-cyano) formazan, Stilbazochrome II, and 4-(2-thiazolylazo) resorcinol, the rest are in the non-azo group. It can be seen that azo compounds are not widely used as metallochromic indicators for scandium comparing to those in non-azo group. This may be due to that the azo reagents give lower sensitivity. For this reason, the author decided to carry out a work in searching for a new azo compound which might be a potential metallochromic reagent for scandium compared to various azo compounds as recorded previously.