CHAPTER — III

ELECTROLUMINESCENCE SPECTRA AND MECHANISM OF ELECTROLUMINESCENCE

ELECTROLUMINESCENCE SPECTRA AND

MECHANISM OF ELECTROLUMINESCENCE

3.1　　　　R E S U L T S:

The metallo complexes of 8- hydroxyqⁿinoline (oxine)of some metals have been prepared and tested for　　their electroluminescent behaviour as described earlier.

It is observed that metallo - oxinates of Mg,Ca,Zn, Cd, and Al were intense electroluminescent,but those of Fe, Co,Ni, Cu,Mn,Cr,Sn and Hg were found to be non-electroluminescent.

The spectral intensity distribution of EL.emission (EL-Spectra) of these electroluminescent metallo-oxinates at various excitation voltages and frequencies are given in the table Nos. 1 - 5 and graphically presented in fig. Nos. 3 - 7. It is evident from the fig.Nos. 3-7 that there is no noticeable change in visible colour and EL.spectra of these oxinates.

For all the metal oxinates studied, the EL-spectra are found to be identical with their normal fluorescence spectra,[133-136] within the experimental limits. Examination of these E_L - spectra reveal that in every case no additional bands to the normal fluorescence spectrum of the oxinate are observed in the spectral region studied. The spectrum of the emitted light output from these compounds consists of a rather intense broad bands peaking at 490 nm, 475 nm,515 nm,

TABLE NO.1   SPECTRAL INTENSITY DISTRIBUTION OF EL. EMISSION (EL. SPECTRA) OF MAGNESIUM OXINATE AT DIFFERENT VOLTAGES AND FREQUENCIES.

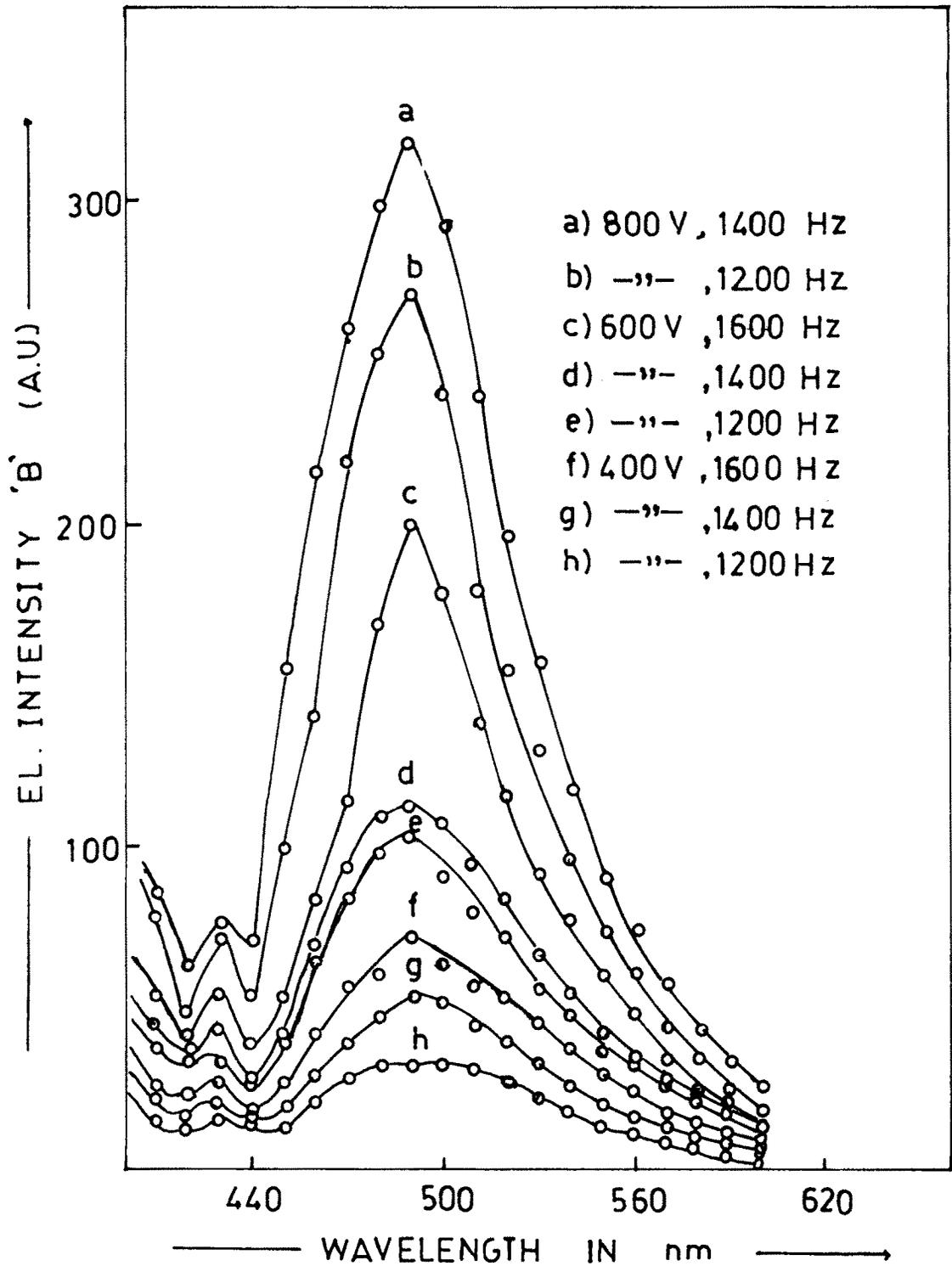| Wavelength of El. emission (nm)	El. Intensity 'B' (A.U.).							
	400 Volts			600 Volts			800 Volts	
	1200 Hz	1400 Hz	1600 Hz	1200 Hz	1400 Hz	1600 Hz	1200 Hz	1400 Hz
410	14	22	26	38	44	56	79	86
420	14	18	24	34	38	42	50	66
430	16	22	28	34	44	56	71	78
440	12	16	18	26	30	40	55	70
450	14	20	28	40	42	54	100	156
460	22	30	42	66	70	86	142	218
470	30	40	56	84	96	116	219	260
480	32	48	53	98	110	170	253	300
490	34	56	74	104	114	200	271	318
500	32	50	64	92	108	180	240	292
510	32	44	58	80	94	140	180	240
520	28	40	54	72	84	116	155	198
530	24	34	46	56	68	92	130	156
540	18	26	38	48	54	78	96	118
550	16	20	30	36	42	60	74	90
560	12	16	24	30	36	48	61	76
570	8	12	18	26	28	34	45	58
580	6	10	16	20	22	26	34	44
590	4	8	12	16	18	18	24	32
600	2	6	8	12	14	14	19	26

FIG·3 ELECTROLUMINESCENCE SPECTRA OF MAGNESIUM OXINATE AT DIFFERENT VOLTAGES AND FREQUENCIES.

TABLE NO.2   SPECTRAL INTENSITY DISTRIBUTION OF EL. EMISSION (EL. SPECTRA) OF CALCIUM OXINATE AT DIFFERENT VOLTAGES AND FREQUENCIES.

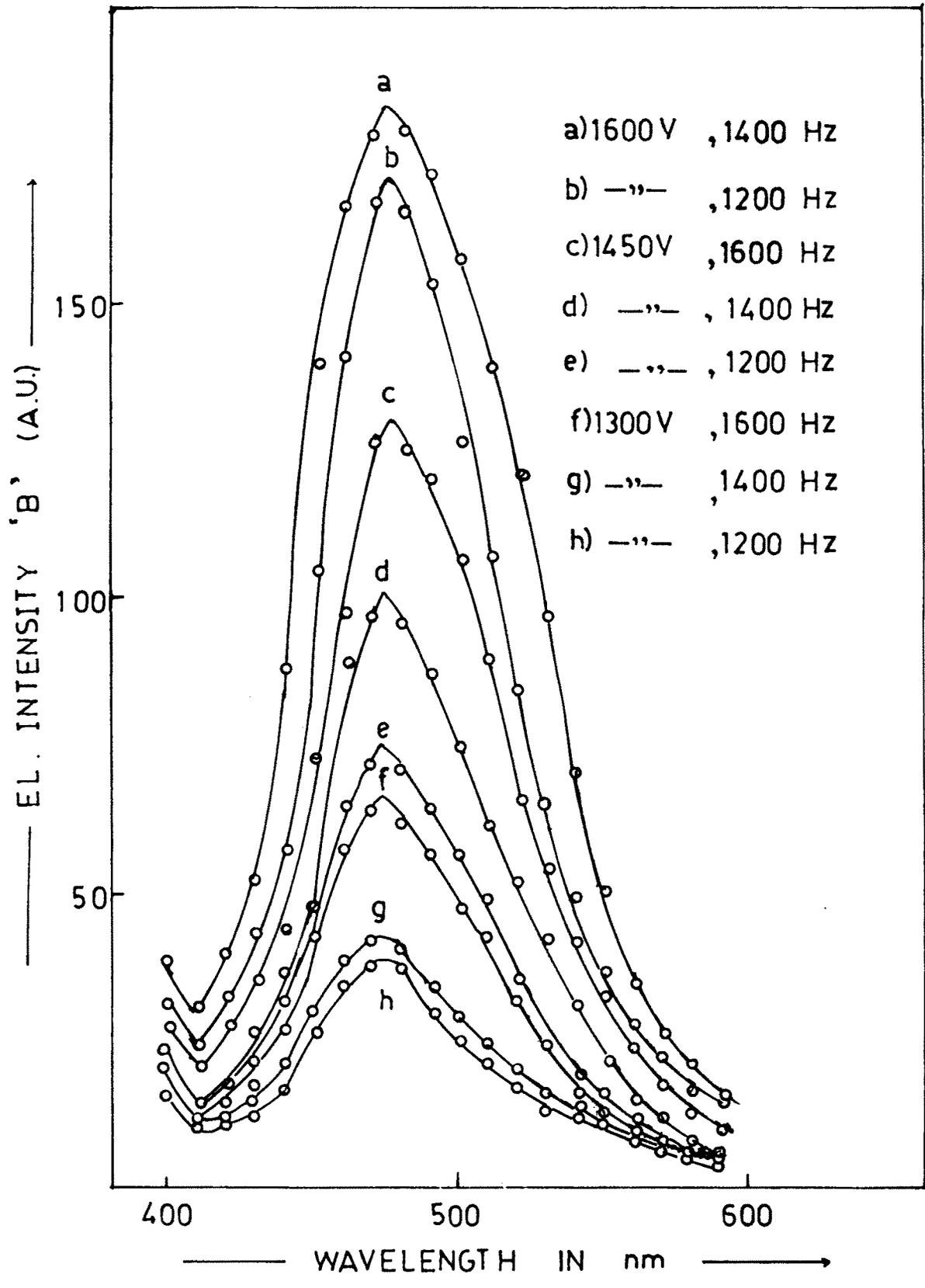| wavelength of El. emission (nm)	El. Intensity 'B' (A.U.)							
	1300 Volts			1450 Volts			1600 Volts	
	1200 Hz	1400 Hz	1600 Hz	1200 Hz	1400 Hz	1600 Hz	1200 Hz	1400 Hz
400	16	18	21	21	24	28	32	38
410	11	12	12	12	15	21	25	31
420	11	12	15	13	18	27	31	40
430	13	15	22	18	27	36	45	53
440	17	21	31	27	37	44	57	88
450	27	30	43	47	47	74	105	140
460	35	39	58	65	90	98	141	167
470	38	42	65	72	97	127	168	179
480	37	41	63	71	96	126	166	180
490	30	35	57	65	88	121	154	173
500	26	29	48	56	75	106	129	157
510	22	25	43	49	62	90	107	140
520	18	21	32	36	53	67	85	122
530	14	17	25	25	43	55	66	97
540	13	15	21	17	32	43	52	71
550	11	12	17	14	22	33	37	51
560	9	10	13	12	16	24	29	37
570	7	8	12	9	12	19	23	27
580	6	6	7	7	9	14	17	22
590	4	5	6	6	7	11	14	17

FIG·4 ELECTROLUMINESCENCE SPECTRA OF CALCIUM OXINATE AT DIFFERENT VOLTAGES AND FREQUENCIES.

TABLE NO. 3 SPECTRAL INTENSITY DISTRIBUTION OF EL. EMISSION (EL. SPECTRA) OF ZINC OXINATE AT DIFFERENT VOLTAGES AND FREQUENCIES.

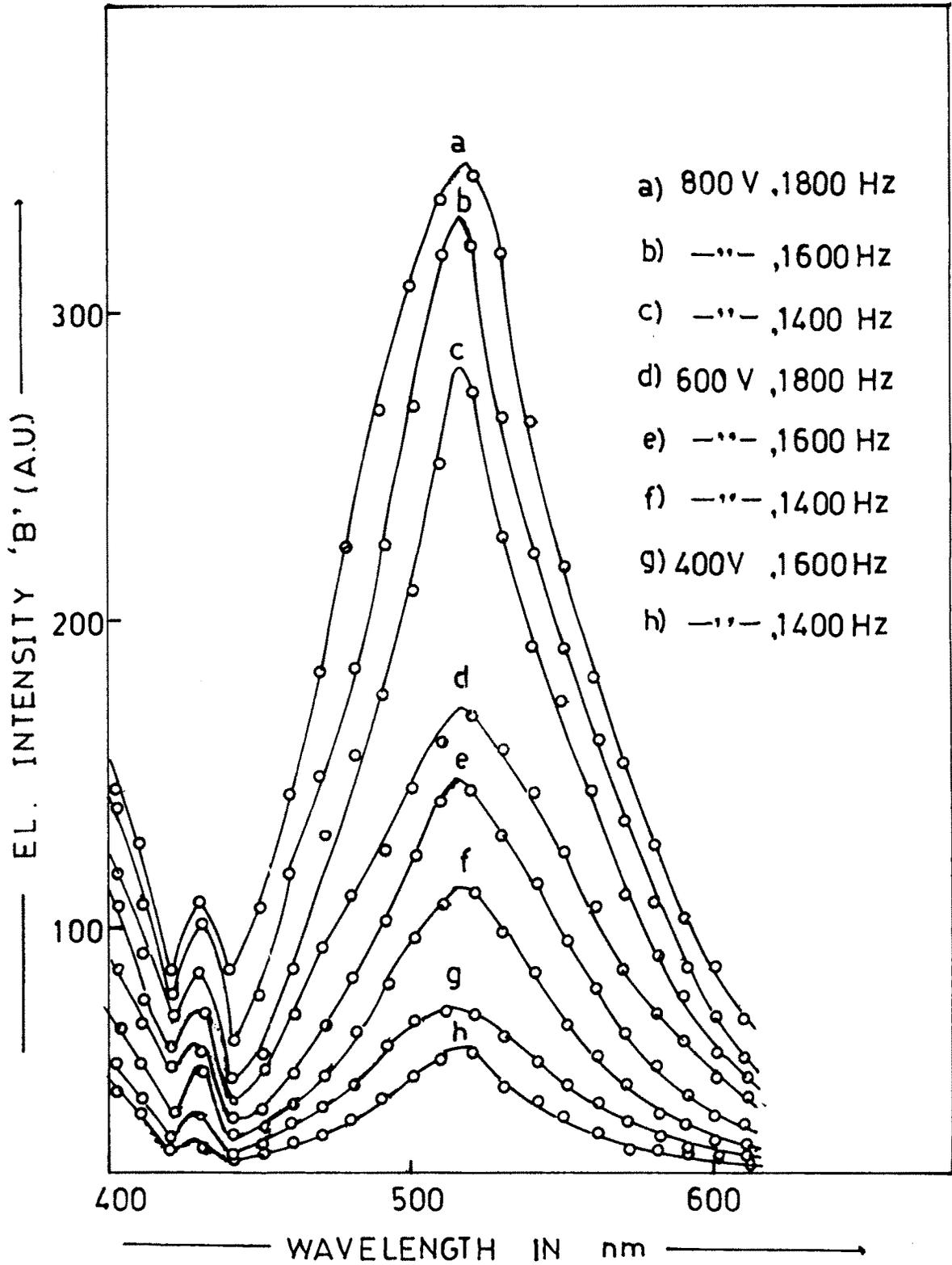| Wavelength of EL. emission (nm)	El. Intensity 'B' (A.U.)							
	400 Volts		600 Volts			800 Volts		
	1400 Hz	1600 Hz	1400 Hz	1600 Hz	1800 Hz	1400 Hz	1600 Hz	1800 Hz
400	50	58	70	88	110	121	142	147
410	41	45	56	69	76	92	108	125
420	28	30	41	56	68	73	76	88
430	34	40	57	60	74	84	102	108
440	24	28	32	39	52	54	62	85
450	25	30	34	40	54	59	78	107
460	26	36	43	53	72	85	118	145
470	30	42	52	68	95	124	148	182
480	32	49	67	84	101	155	184	223
490	36	59	81	103	126	178	224	268
500	44	68	96	123	145	210	270	309
510	52	72	109	142	160	252	320	338
520	56	71	111	146	169	274	322	343
530	60	64	100	130	158	229	266	320
540	48	56	86	115	143	193	222	262
550	44	49	68	96	123	172	190	218
560	39	44	59	82	106	144	159	182
570	34	35	48	67	86	103	135	154
580	29	32	43	55	73	90	108	129
590	27	29	35	46	64	78	90	103
600	26	27	33	40	52	59	73	88
610	24	25	30	37	47	52	57	70

FIG·5 ELECTROLUMINESCENCE SPECTRA OF ZINC OXINATE AT DIFFERENT VOLTAGES AND FREQUENCIES.

TABLE NO. 4   SPECTRAL INTENSITY DISTRIBUTION OF EL. EMISSION (EL. SPECTRA) OF CADMIUM OXINATE AT DIFFERENT VOLTAGES AND FREQUENCIES.

wavelength of EL. emission (nm.)	El.Intensity 'B' (A.U.)							
	400 Volts			600 Volts			800 Volts	
	1200 Hz	1400 Hz	1600 Hz	1200 Hz	1400 Hz	1600 Hz	1200 Hz	1400 Hz
410	27	36	42	63	60	63	70	80
420	23	30	37	55	48	55	61	77
430	17	28	31	47	38	47	50	70
440	13	23	27	37	31	38	40	64
450	12	20	23	34	28	35	37	54
460	13	18	22	35	29	37	43	58
470	18	20	26	39	36	42	55	73
480	19	27	32	43	47	52	65	89
490	24	32	40	51	55	61	77	104
500	27	38	47	58	65	73	92	120
510	31	44	55	68	77	85	114	147
520	38	53	64	74	84	97	126	177
530	34	47	54	67	75	86	104	139
540	26	39	49	59	68	74	88	125
550	24	33	42	54	63	65	76	110
560	23	29	37	46	55	58	67	100
570	21	25	34	41	46	50	59	78
580	18	21	29	35	38	43	48	57
590	16	18	26	28	32	35	40	48
600	14	16	22	24	26	28	32	38
610	12	14	17	17	20	22	25	30
620	10	12	13	13	15	16	18	22

a) 800 V , 1400 Hz

b) —"— ,1200 Hz

c) 600 V ,1600 Hz

d) —"— ,1400 Hz

e) —"— ,1200 Hz
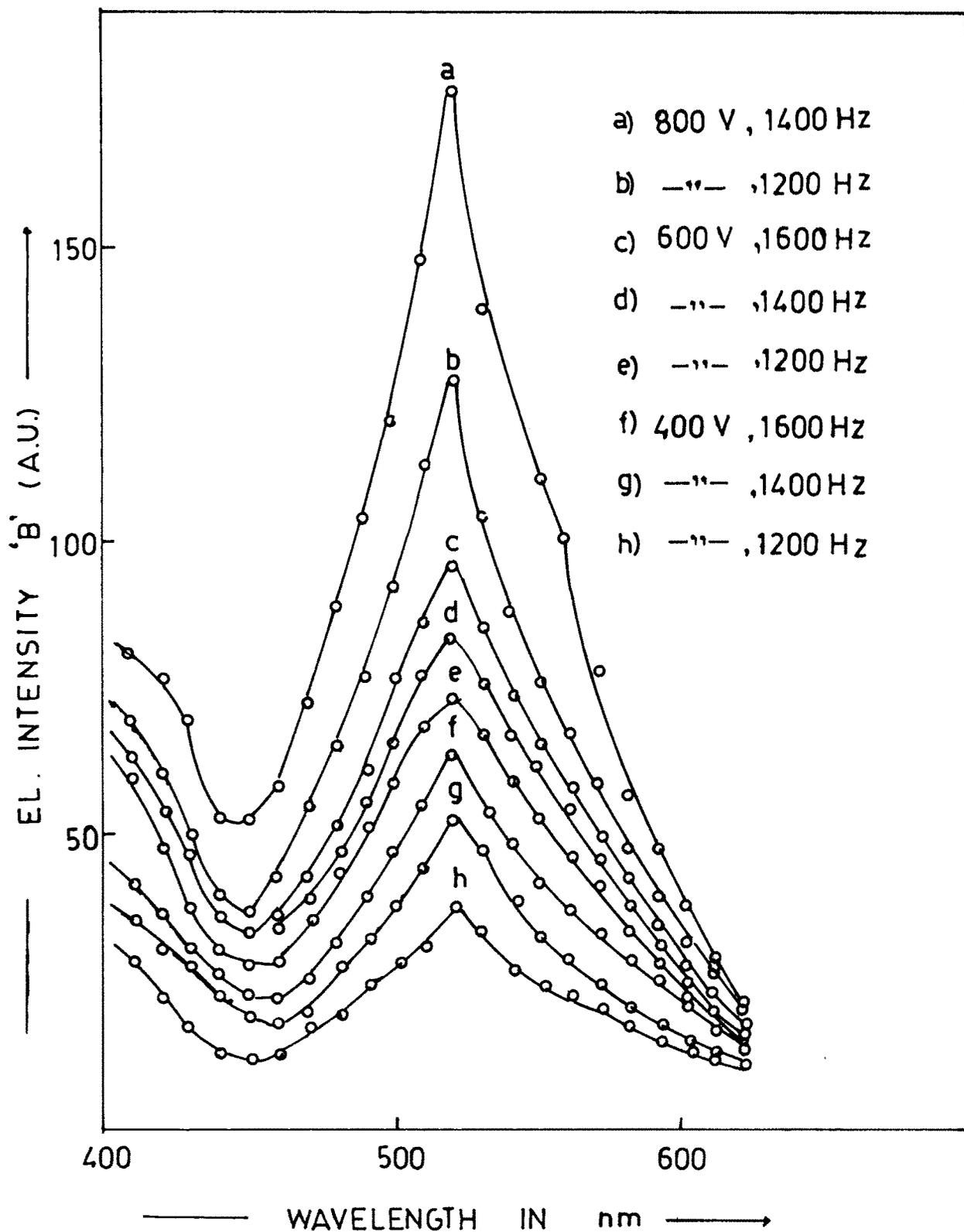
f) 400 V ,1600 Hz

g) —"— ,1400 Hz

h) —"— ,1200 Hz

FIG·6 ELECTROLUMINESCENCE SPECTRA OF CADMIUM

OXINATE AT DIFFERENT VOLTAGES AND

FREQUENCIES.

TABLE NO. 5 SPECTRAL INTENSITY DISTRIBUTION OF EL. EMISSION (E$_1$. SPECTRA) OF ALUMINIUM OXINATE AT DIFFERENT VOLTAGES AND FREQUENCIES.

| Wavelength of EL. emission (nm)	EL. Intensity 'B' (A.U.)							
	400 Voltes		600 Volts		800 Volts		1000 Volts	
	1000 Hz	1500 Hz	1000 Hz	1500 Hz	1000 Hz	1500 Hz	1000 Hz	1500 Hz
400	10	31	45	72	76	76	82	96
410	8	25	41	69	72	70	79	86
420	6	17	20	32	41	43	50	72
430	6	19	34	52	62	53	68	95
440	5	11	15	26	39	40	52	56
450	5	11	12	24	27	27	32	52
460	7	14	19	31	33	38	46	55
470	8	19	26	37	44	56	69	73
480	10	22	35	44	54	74	86	98
490	13	27	40	51	67	90	107	130
500	15	28	49	57	81	108	116	155
510	16	32	59	63	95	114	122	176
520	16	31	49	62	84	106	115	151
530	14	28	41	59	74	100	111	125
540	13	26	34	54	64	80	94	106
550	11	23	27	46	53	71	78	95
560	9	19	23	40	44	57	64	83
570	7	16	18	35	38	46	51	76
580	6	14	11	29	32	37	42	54
590	6	13	10	26	27	30	34	44
600	5	11	9	22	24	24	24	34
610	5	9	7	18	20	20	21	26
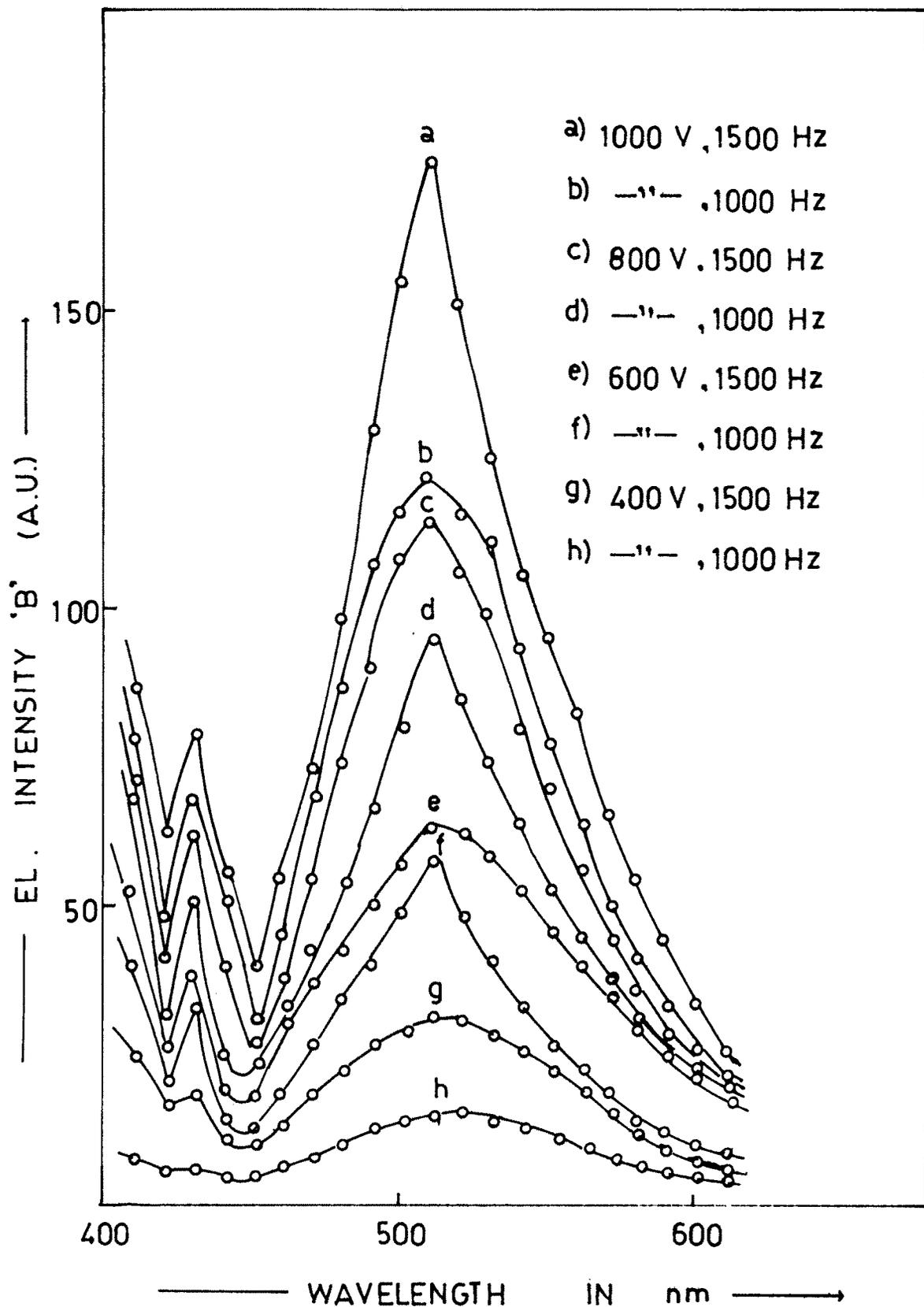
FIG·7 ELECTROLUMINESCENCE SPECTRA OF ALUMINIUM OXINATE AT DIFFERENT VOLTAGES AND FREQUENCIES.

520 nm and 510 nm for Mg,Ca, Zn,Cd and Al oxinates respectively, having a half band -widths invariably greater than 70 nm at room temperature.

In addition to above observations,no spectral shift was noticed with change in voltages and frequencies of the excitation field as it is observed in many inorganic systems. Thus, it seems that the band positions in all these oxinates are independent of excitation voltages and frequencies.

Electroluminescence from variety of fluorescent organic compounds has been studied by number of workers,but from survey of the literature,it seems that no work has been so far done on electroluminescent properties of these metallo-oxinates and therefore,we belive that this is the first report on EL. of these complexes.

In addition, other important results,which are evident from our experimental observations are:

i) In general, the intensity of EL. emission of metal complexes varies with the metal ion, decreasing with increasing atomic number. Also,within one period- that is a group of diamagnetic nontransition metal ions the complexes seems to exhibit reasonably smooth treads in the intensity of EL. emission.

ii) For the complexes of oxine with the metal of group II A (Mg and Ca) and II B (Zn and Cd),general expectation of decreasing intensity with increasing atomic number is followed.

iii) The metallo- complexes of group II A (Hg & Sn) are found to be non-electroluminescent.

iv) The divalent paramagnetic Cr (II),Mn(II),Co(II), Ni(II) and Cu (II) complexes and trivalent paramagnetic Fe(III) complex do not show electroluminescence.

v) The trivalent diamagnetic Al complex of oxine was found to be good electroluminescent.

3.2   D I S C U S S I O N :

A great variety of metal complexes,including the porphyrins, chlorophylls,hydroxyquinolines,Phthalocyanines and others have been reported to be highly luminescent compounds.

The broad considerations for the important processes affecting the luminescence of metal chelates are

a) the nature of the ligand,

b) the nature of the metal,

c) the nature of the perturbation- that is,does the metal perturb the ligand levels or does the ligand perturb the metal levels,

d) intramolecular energy transfer processes,

e) solvent and temperature effects,etc.

In the first area,obviously important are the emission characteristics of the uncomplexed parent molecule.With regard to the metal,important points are its position in the periodic table- categories include the transition elements, the rare earths and the remainder.In addition, the diamagnetic or

paramagnetic nature of the metal ion and its oxidation

state are of great importance,as is the third factor,since

the nature of the excited states and their intercombination

are largely determined by the nature of the perturbation.

The possibility of intramolecular energy transfer can

notably alter the nature of the emission. This is particu-

larly true for rare-earth chelates. The temperature is

particularly important because of its effect on the colli-

sional deactivation of excited states and thus both the

intensity and nature of the emission. Also, the temperature

affects the fine structure character of the emission.

The effect of metal ion on the luminescence of

porphyrins has been studied experimentally and theoretically[137-138]

and the porphyrin work provides a framework in which the

results of the present study may be interpreted.

The Excitation step is almost always the absorption

of a photon by the chelate to produce π , π^* excited

state of the ligand. Internal conversion to the lowest

vibrational level of the first excited electronic state very

quickly follows (ca. 10^{-12} s)[139]. If internal conversion occurs

to a large extent,most molecules return to the ground state

without emission and the chelate will be non-luminescent.

If the excited species contains a paramagnetic atom (the

metal ion in many chelates), it usually will not luminesce

because, the rate of intersystem crossing is greatly increased

by paramagnetic species. The extent of intersystem crossing

also depends on the atomic number of atoms in the EL.

material. Heavier atoms increase spin-orbit coupling which

leads to an increase in the rate of intersystem crossing.

Unless all excitation energy has been dissipated by

one or more of the above processes, the return of the metal

chelate compound to the ground state (after ca.10^{-8} S)

will be accompanied by emission of luminescence radiation.

Most luminescent metal chelate compounds emit upon making

the reverse transition that was made upon excitation,i.e.

$\pi^* \longrightarrow \pi$. Because of the nature of the combining states,

the emission spectrum of a typical luminescent metal chelate

will consist of a rather broad band having a half band-width

greater than ca. 2000 cm^{-1} (ca.60 mμ or nm) at room temperature.

Under certain conditions, the metal chelate may emit

luminescence denoted as $m^* \longrightarrow m$. Subsequent to energy

transfer, if some excitation energy has passed to a resonance

level of the metallic ion, a radiative transition may occur

from the resonance level(s) to the ground state. Because this

pathway involves a radiative combination of atomic orbitals,

luminescence would be characterized by a relatively narrow

bandwidth.

Electroluminescent spectra reported by us for all the

compounds (Fig. Nos. 3-7)consists of a rather broad bands,

having a half band widths invariably greater than 70 nm.

Thus, it seems that the appearence of these bands may be due

to $\pi^* \longrightarrow \pi$ transitions only.

The important role of the $\pi \longrightarrow \pi^*$ transition in the sequence of events leading to emission by most luminescent metal chelates has been given great importance; it is hardly surprising that a ligand which forms luminescent chelates usually has π electrons. It is not only necessary that the ligand to have a aromatic character.

Weissman and recently Crosby and [140-141] coworkers have studied intramolecular energy transfer from the ligand to the metal in rare earth ion chelates when excitation occured by a $\pi \longrightarrow \pi^*$ transition on the ligand.

Paris[142] has pointed out that " Charge transfer " luminescence may be expected for (diamagnetic) transition metal ion chelates when the metallic ion is not too difficult to oxidize, and the ligand produces large ligand field splitting.

Metallic ion plays an important role in the luminescence charactaristics of a metal chelate.Only those ions which are diamagnetic when co-ordinated and are not themselves easily reduced can expected to form luminescent metal chelate compounds. Stevens[8] showed that only those metallo -oxinates containing a metallic ion which has its outer electronic subshell filled would lumminesce. Yuster and Weissman[143] have explained the luminescence on the basis of varying degrees of interaction between the optical electrons in the complex and field of metal ion. Complete electron shells afforded more protection than empty shells against perturbation and dissipation of lumminescence.

The oxinates of group II A (Mg,Ca), group II B

(Zn,Cd) and group III A (Al) are observed to be good

electroluminescent while the oxinates of incomplete shells

or a transitional nature are observed to be non-electrolumine-

scent. These observations are in accordance with the Yuster

and Weissman, and Stevens.

The concept of radiationless transition as a result

of geometrical distortion is supported by a general consi-

deration of the data on the luminescence of the complexes

with the metals of group II B(Zn,Cd). In group II B

complexes, the luminescence intensity of Cd derivative is

much less than that of the Zn complex, while in Hg metal

atom has a very large ionic and convalent radii and its

complex is non-luminescent. It is clear that with increasing

size of the metal, the rate constant increases for one or

more modes of radiationless deactivation to the ground state.

The distortion factor plus the high atomic number provide

quenching mechanism for the luminescence via ISC to the

triplet state and IC to the ground state from both the

singlet and triplet states.

In the Zn and Cd comparision, the overall EL.intensity

appears to decrease with increasing ionic size. Here,again,

molecular distortion resulting from the size of the Cd

ion may play an important role.

The relationship between luminescence ability and
144-145
chemical structure has been considered by several investigators.

The possibility of a stereochemical effect seems worthy of

mention in accounting for the failure of certain chelates to

luminesce. Although stereochemical information on the metal oxinates in scanty, zinc is reported to form a tetrahedral complex with oxine (sp^3 - orbitals). Complexes of magnesium, calcium and cadmium are often tetrahedral, whereas the divalent transition metals-copper (II), nickel, cobalt, and manganese, usually forms square planar complexes. The trivalent oxinate i.e. aluminium have an octahedral ($d^2 sp^3$) arrangement of the ligands. On the basis of these observations and our results, the square planar configuration of ligands is suggested as a Possible cause of the failure of certain oxinates to luminesce at room temperature.

3.3   MECHANISM OF ELECTROLUMINESCENCE.

Electroluminescence spectra of all the prepared metal-oxinates were studied by using an EL.cell as described earlier (Chapter- II, 2.3-a).

In our study, at first on visually observing the emitted radiations from these compounds, it was thought that genuine El. was being observed. However, examination of El- spectra of these compounds revealed that in every case the spectra obtained were exactly identical with the reported normal fluorescence[133-136] and photoluminescence[146] spectra. The emitted radiation showed charactaristics similar to the cells containing inorganic phosphors, with the exception that higher voltages were needed to stimulate emission.

In order to know the exact nature of El. emission in
metal- oxinates, attempts have been made to excite the
metal-oxinates in presence of various dielectric materials
such as castor oil, silicon oil,high vacuum grease and
transformer oil. In every attempt care was taken to exclude
the air completely. It was observed that in presence of all
these dielectric materials the intensity of emitted light
was too low to be measured. However, when the metal-oxinates
were excited without dielectric material very intense El.
was observed. From these observations we think that the
traces of air present in the cell may be playing an important
role in El. emission. In addition, our experimental observa-
tions are similar with the observations reported by different
workers for various organic compounds, the results of which
are explained on the basis of glow discharge mechanism.When
high electric field is applied between the two electrodes,
breakdown of the gas surrounding the cell can occur,resulting
in light emission from the gas and if a fluorescent material
is present, the light emitted by the gas can cause photoe-
xcitation of the material in the cell. This is a particularly
common mechanism of " El." for organic compounds.

As discussed earlier (Chapter-II,2·2), the oxinates
of Mg,Ca,Zn,Cd and Al and are found to be highly photolumi-
nescent, while oxinates of Mn,Cr,Fe,Co,Ni,Cu,Hg and Sn are
non-photoluminescent. These compounds when tested for their
El. behaviour it was found that only the photoluminescent

oxinates show bright El. emission while the non-photolumines-
cent oxinates were non-electroluminescent. These facts strongly
supports the validity of glow discharge mechanism of El.
emission from our metallo- complexes of 8-hydroxyquinoline.

In glow discharge mechanism, nitrogen molecules from the
air gets excited and emit ultraviolet (U.V.) radiations.
These U.V. radiations excite the fluorescent material which
latter on emits the normal fluorescence emission.

Short and Hercules[35] studied the El. of a variety of
fluorescent organic compounds. Spectral observations showed
the emitted radiation to be identical with normal fluorescence
spectrum. In addition nitrogen bands were invariably present
in spectra taken in air. They explained the origin of radiation
emitted by an El. cell on the basis of glow discharge mecha-
nism. In our observations, the absence of the emission bands
due to second positive series of nitrogen may be attributed
to the high absorbance of the mica which we have used as the
insulator in the El.cell. The decreasing light out-put of
given cell with time can be attributed to the chemical action
of radicals generated in the glow discharge on the surface of
phosphor.

The general and some what surprising, effect of the
glow emission mechanism is that the electrical properties
exhibited are very similar to those observed for genuine
inorganic El. which will be evident from our study on
frequency and voltage dependence of El. emittance (Chapter-IV).

It is this fact that has led to most of confusion with regard to differentiating between glow discharge excitation and true El. of organic compounds. So we think that the mechanism of process involved in light emission in metal-oxinates must be due to glow discharge excitation mechanism.

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