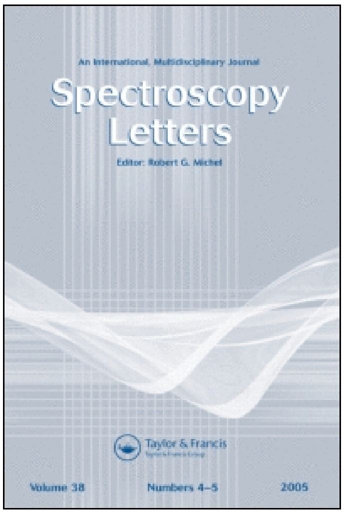

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REE SPECTRAL LINES FOR THE DETERMINATION OF EXCITATION TEMPERATURE IN ANALYTICAL PLASMAS

BY

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ABSTRACT

The spectra of rare earth elements (REE) have been investigated to select thermometric species for spectroscopic diagnostic of analytical plasmas. Groups of lines of Y II, La II, Eu II and Yb II were found appropriate for the determination of ionic excitation temperature in argon wall-stabilized plasma arc (WSA) and inductively coupled plasma (ICP). Boltzman plots with excellent Fitting to straight lines were obtained. Temperature values deduced with the different groups of spectral lines agree with each other as well as with that obtained with the most familiarly used Ti II lines.

1- INTRODUCTION:-

For analytical plasmas, the temperature is considered as one of the most important parameters used to characterize the state of the plasma. An accurate knowledge of the temperature, actually experienced by the analyte species leads to understand the processes occurring in the plasma namely, solute vaporization, dissociation, atomization and ionization. A recent summary of the diagnostic techniques for temperature determination is given by Wiese (1).

The excitation temperature of certain species atomic or ionic can be determined from the measurement of the intensity of its spectral lines assuming

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that the population of the energy states of the species follows Boltzman distribution law .This can also be applied to plasmas in partial L T E, consequently the intensity of the spectral line is given by

$$\mathrm{I} = \int I\lambda \, d\lambda$$

$$= \frac{hc}{4\pi\lambda_{nm}} \cdot \lambda_{nm} . l . A_{nm} . N_{o(T)} \cdot \frac{g_n}{z_{(T)}} e^{-E_n/KT_{exc}}$$

where :h is planks constant λ_{nm} is the wavelength, *l* is the thickness of the plasma layer, A_{nm} is the transition probability, $N_{o(T)}$ is the total density of species in the concerned ionization stage, g_n is the statistical weight, $Z_{(T)}$ is the partition function, E_n is the excitation energy of the upper level (n), K is Boltzman constant and T_{exc} is the excitation temperature.

This equation can be applied using absolute intensity of one spectral line provided that the other atomic constants including No(T) are accurately known or the intensity ratio of two spectral lines for which $N_{o(T)}$ and $Z_{(T)}$ cancel. A more widely used method is based on measuring the intensity of a group of spectral lines of one and the same ionization stage. Plotting log Iλ/gA versus E_{exc} should yield a straight line (which is known as the Boltzman plot) with a slope proportional to $1/T_{exc.}$.Deviation from the straight line means deviation from Boltzman distribution law.

In the literature there are certain elements which are traditionally used as thermometric species. In fact a thermometric element should posses relatively high ionization potential so that its addition should not affect the state of the plasma. Iron atom and titanium ion are the most widely used species for the determination of atomic and ionic excitation temperature respectively (2-5). Vanadium, Uranium and Zinc have been also used by different investigators as appropriate thermometric species (3,6,7) In the present laboratory two plasmas have been used as excitation sources for optical emission spectrometry. These are the inductively coupled plasma (ICP) and the wall- stabilized argon arc (WSA) which is a home made device.

The determination of the REE in geological materials as phosphates or black sand deposits have been for a considerable time the field of interest (8-10) . The experience with the rare earth spectral lines initiated the interest to study the possibility of their application for the determination of the excitation temperature.

Table I- Spectral lines and their atomic data

La			EU			Y			Yb			Ti		
λ(nm)	E(cm^{-1})	gA	λ(nm)	E(cm^{-1})	gA	λ(nm)	E(cm^{-1})	gA	λ(nm)	E(cm^{-1})	gA	λ(nm)	E(cm^{-1})	gA
373.58	28155	0.019	374.13	37849	1.1	360.07	29214	5.3	345.40	55702	17	321.70	31301	-0.48
375.90	28565	1.5	374.35	36628	0.24	360.19	28595	2.8	347.63	28758	.024	321.82	43741	0.43
373.71	53333	27	376.11	37224	0.69	361.10	28730	3.6	347.88	58961	22	322.28	31114	-0.41
378.06	32161	0.21	376.59	36628	0.21	363.31	27512	2.6	352.02	58961	10	322.42	43781	0.40
378.48	26414	0.023	378.87	53490	5.6	366.46	28730	1.3	354.98	61215	5.1	322.86	39675	0.24
379.08	27388	1.7	379.15	37011	0.12	366.84	55645	13	356.03	49498	3.0	323.22	39927	0.07
379.08	28315	2.3	379.90	36628	0.29	371.03	28394	5	357.05	61051	4.4	323.45	31301	0.31
380.87	29498	0.056	381.96	26173	4.8	374.75	27517	0.37	358.54	49301	5.2	323.65	31114	0.19
383.50	31786	0.26	382.66	52963	15	377.43	27532	3.2	361.98	56376	5.4	323.90	30959	0.06
384.07	27424	0.24	391.07	27256	4.7	377.65	27517	0.43	363.77	48900	2.3	323.96	39603	-0.15
384.60	27388	0.047				378.23	55645	16	369.41	27026	.74	324.19	30837	-0.14
348.90	25973	0.42				378.87	27227	2.1						
385.49	32161	0.19												
386.44	54435	28												
387.16	26838	1.1												

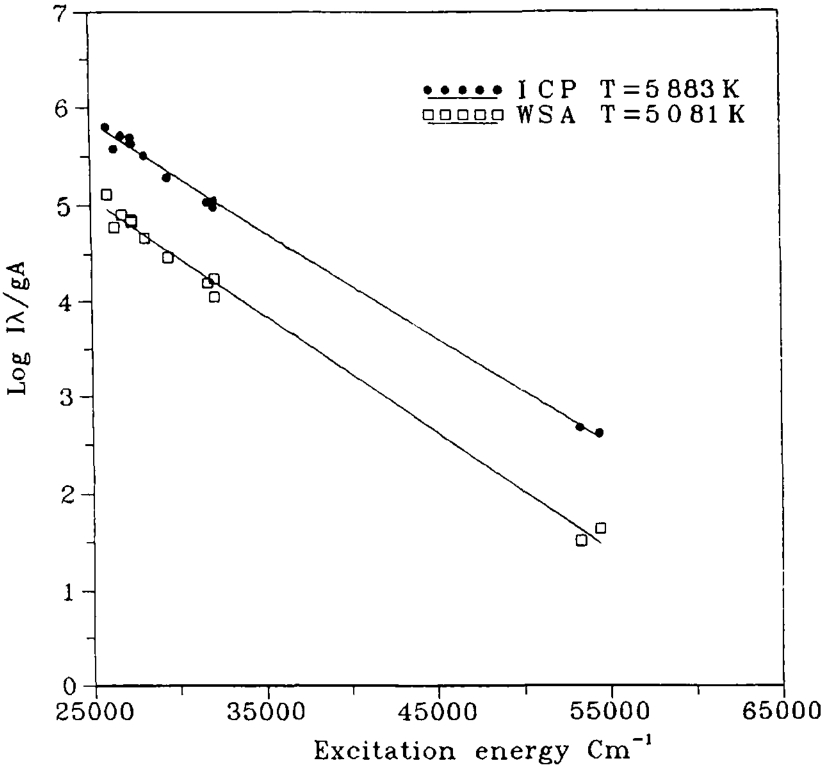

Figure (1) Boltzman plots of La II Lines

2-EXPERIMENTAL

2-1. The Excitation Sources.

2-1.1. The wall- stabilized plasma arc.

The construction of the wall- stabilized plasma arc has been described in detail in previous papers (8).An argon arc is struck between two water- cooled electrodes; a pointed tungsten rod cathode and a tungsten ring anode in a channel of 5 mm diameter formed by axial holes in water cooled brass segments. The middle part of the arc has a wider diameter of 25 mm and serves as the analytical chamber. It is fitted with a quartz window for observation and its lower part is provided with a channel for the tangential introduction of aerosol of the sample to be excited. A cross flow nebulizer (Beckman), is used for generation of the sample aerosol. An argon stream is introduced at the cathode segment which serves as the plasma gas as well as an extra coolant for the cathode. When the argon arc is struck, its column, observed in the analytical chamber is constricted by the thermal pinch effect. Under this condition aerosol particles are reflected at the hot boundaries of the plasma. No effective aerosol introduction into the plasma is achieved unless the sample contains a relatively high concentration of an easily ionizable element. Potassium chloride is used for this purpose. In this case the intense constricted argon arc column becomes more wider in diameter and less intense. Its temperature drops to about 5ooo K (5). Under these conditions the aerosol penetrates easily into the plasma as observed on the ratio of line- to-background for the different elements.

Compromise optimal working conditions for analytical application with this plasma and with the present nebulizer are :

Arc current	20 A
Carrier flow rate	10 L/min.
Argon flow rate at the cathode	3 L/min.
concentration of KCl in the nebulized solutions	0.75 M.

2 - 1. 2. ICP Equipment :

A free-running FS4 generator with a frequency of 27.12 MHz and a maximum power output of 4 KW (Linn high therm) is used to energize an argon ICP. The ICP torch is a Greenfield type. A Babington type Golk nebulizer is used for aerosol generation and a peristaltic pump (Gilson, Minipulse 2) is employed for the solution feed. All measurements are performed under the working conditions used for the analysis of the REE. These are :

HF power	750 watt
Cooling gas flow rate	16 L/min.
Plasma gas flow rate	3 L/min.
Carrier gas pressure at the end of the nebulizer capillary	3 bar.

2- 2. Spectral Equipments :-

Radiation from either ICP or wall-stabilized arc illuminates a 1-meter Czerny Turner monochromator (Mcpherson 2051) using a three lens intermediate image system. A zone of 4x4 mm. in either sources is selected to fully illuminate

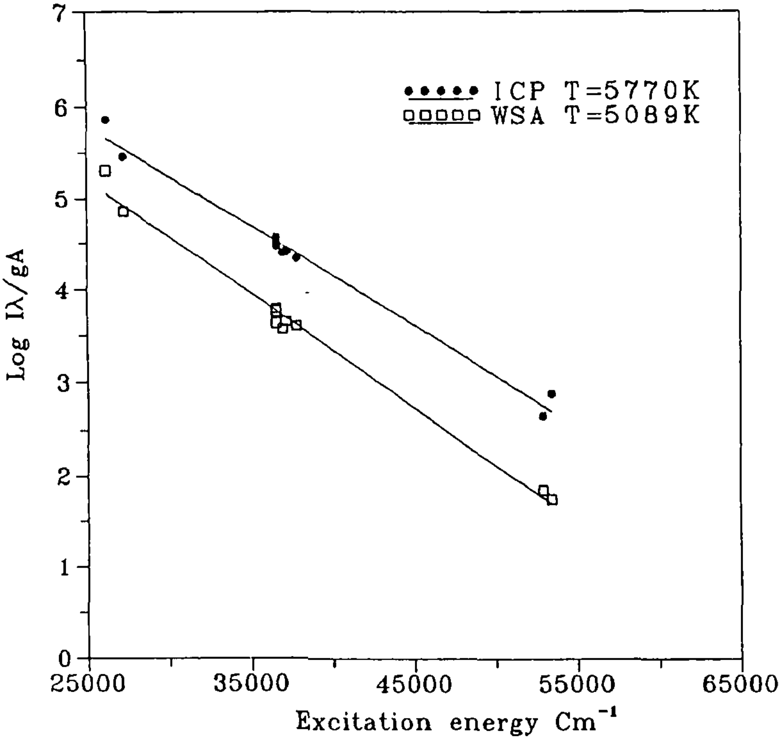

Figure (2) Boltzman plots of Eu II Lines

the monochromator aperture. IN the ICP the observation zone lies at 12 mm above the load coil while in the wall-stabilized arc, it is in the center of the analytical chamber. The monochromator is equipped with a plane grating with grating constant of 1/1200 mm giving reciprocal linear dispersion of 0.83 nm/mm. Both entrance and exit slits are 0.02 mm which enabled a practical band width of 21.6 Pm . For measuring of spectral intensities a Hammamatsu Photo multiplier R300 whose current is amplified using the linear mode of Model 762 Mcpherson logarithmic ratiometer and recorded on a strip chart recorder Hwelett Pachard (Model 7127A). Net line intensity integrated over the line profile are used for all measurements. The spectral response of the whole system for both ICP and WSA are measured using the quartz halogen lamp standard for spectral irradiance ORIEL (model No. 63358) for the spectral region 250-500 nm. The measured

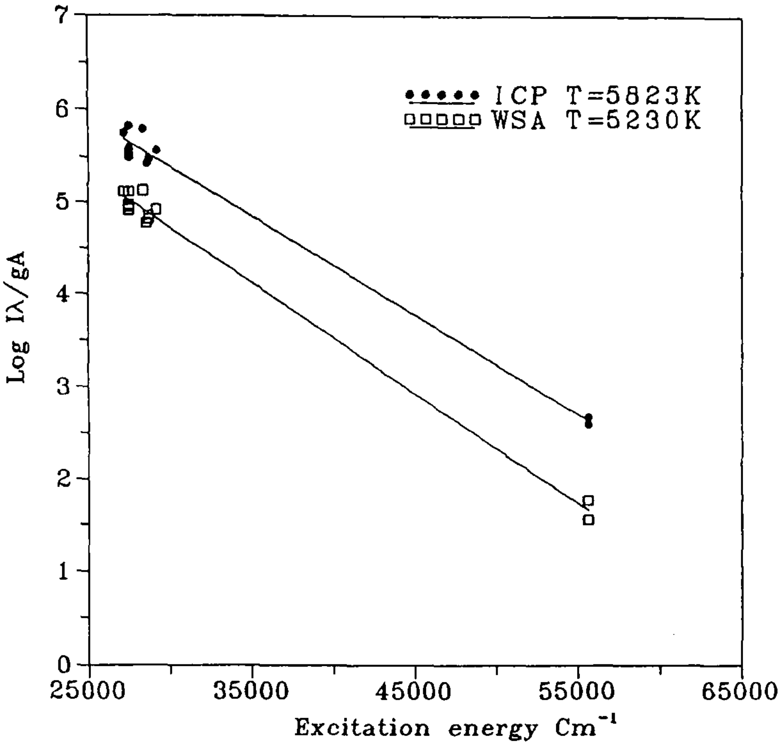

Figure (3) Boltzman plots of Y II Lines

response curve is used for correction of line intensities in the different wavelength regions. It is to be mentioned here that the intensities used in the present work are not Abel-transformed. Jarosz (3) reported that for the central injection Abel transformation is not necessary so long the observation is carried in the upper analytical zone .

2- 3. RE Solutions :

RE solutions were prepared by dissolving spectroscopic pure RE oxides in conc. HNO_3 evaporated to near dryness and completed with bidistilled water to give 1000 μg ml^{-1} stock solutions. Solutions of the individual elements containing 50 μg ml^{-1} were used for generating the spectra of the element. This relatively

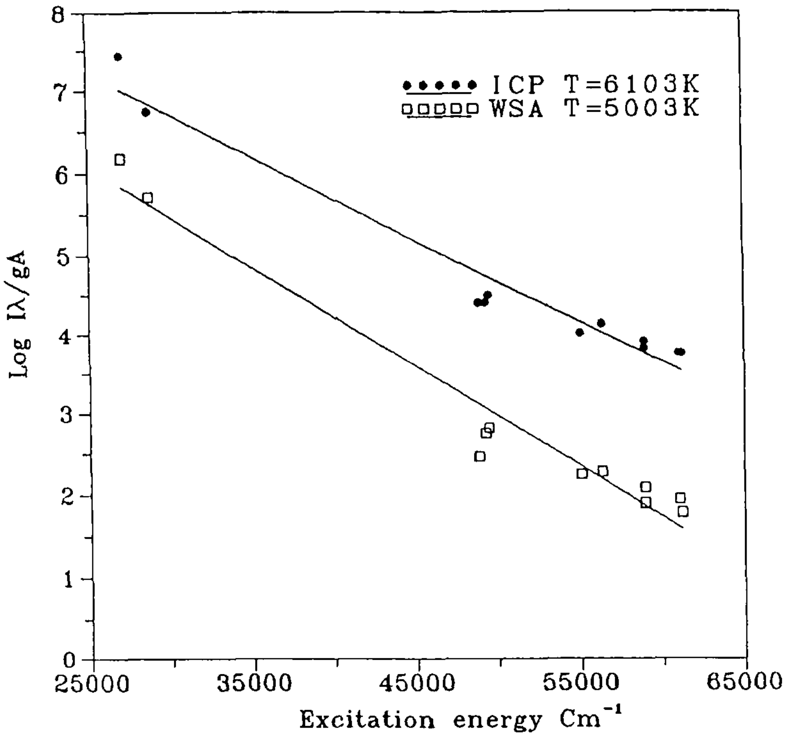

Figure (4) Boltzman plots of Yb II Lines

high concentration was necessary to obtain measurable intensity of the weak lines while not saturating the PM in case of strong lines.

3 - RESULTS and DISCUSSION

3 - 1. Selection of Spectral Lines for Temperature Measurement:

It is well known that the group of spectral lines selected for the construction of Boltzman plot should satisfy certain requirements. The most important of these requirements is that the difference in excitation energy should be large enough to ensure accurate temperature measurement (1-2ev). Their intensities should be sensitive for temperature changes and their intensity profiles should not be influenced by Stark broadening effect and not susceptible to self absorption. The

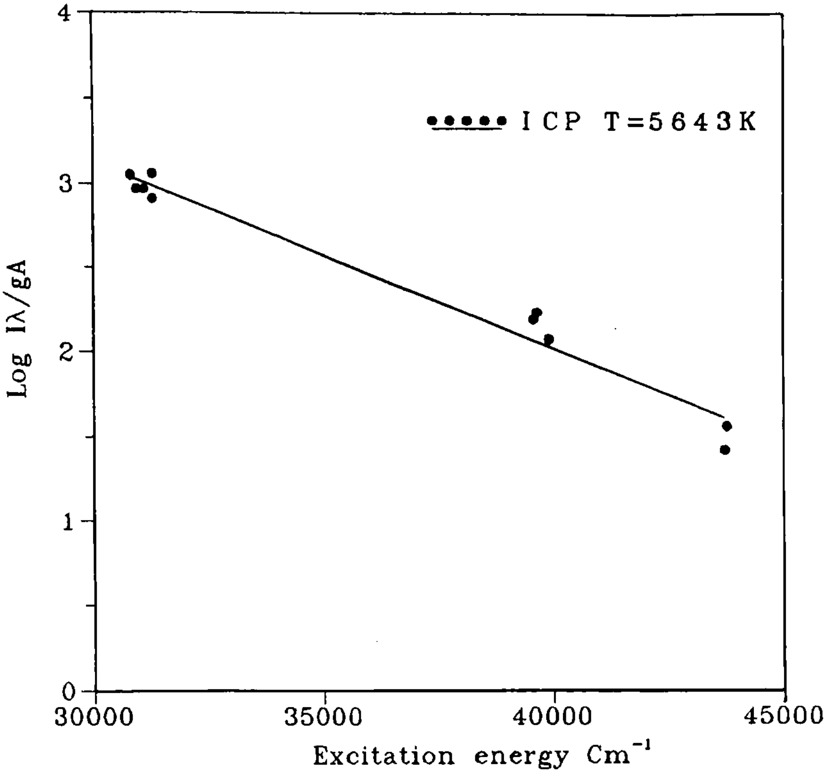

Figure (5) Boltzman plots of Ti II Lines

line should be possibly lie in a narrow wavelength interval. Investigating the atomic data of the rare earth spectral lines showed that these elements posses line rich spectra specially the ionic lines which are predominant in the argon plasmas considered. For some rare earth elements spectral lines with reasonable intensities and having energy differences as high as 28000 cm^{-1} could easily be measured. The only difficulty was the availability of different sources for the transition probabilities. In the present work , gA values after Corliss and Bozman (11) was the only available data which was found appropriate for this purpose. The REE whose lines were found to posses the foregoing requirements are La, Eu, Yb together with Y. The wavelength values as well as the other atomic data of the selected lines are given in table(1).

Table II - Results of temperature measurements in wall-stabilized arc and ICP.

Lines Used	WSA	ICP
Y II	5230 ± 137 K	5823 ± 194 K
La II	5081 ± 127 K	5542 ± 114 K
Eu II	5084 ± 182 K	5777 ± 236 K
Yb II	5003 ± 93 K	6103 ± 422 K
Ti II	4820 ± 200 K	5643 ± 308 K

3 - 2. Boltzman Plots and Results of Temperature Measurements :

Figures (1-5) show the resultant Boltzman plots obtained for WSA and ICP using the selected spectral lines of La II , YbII, YII, Eu II and Ti II respectively. The straight lines obtained indicate the suitability of the selected RE spectral lines for the determination of excitation temperature of the ionic species in both plasmas under investigation. The results are summarized in table (2). The resultant temperature values agree within the determination error with those values obtained using Ti II lines for both WSA (9) and ICP (Fig.5). Again the obtained results indicate that the population distribution of the energy states of the ionic species in both plasmas follow Boltzman distribution law.

Conclusions:

Form the results obtained in the present work, it can be concluded that :

1- The rare earth elements La, Eu, Yb and Y presents suitable thermometric species for the determination of excitation temperature in analytical plasmas working under atmospheric pressure. The ionization potentials of these elements are 5.614, 5.67, 6.25 and 6.6 ev respectively.

2- These elements posses groups of spectral lines with wide range of excitation energies and have reasonable intensities which make them convenient for accurate temperature determination .

3- Except for Yb which gives a relatively high value of excitation temperature for the ICP, the lines of La II, Eu and Y give excitation temperature values which are in good agreement with each other. The excellent fitting of the points to straight lines (Δ T relatively small) ensures the suitability of these lines for temperature measurement. Moreover these temperature values agree with those obtained with the most familiar Ti II lines. Accordingly the above mentioned rare earth lines can be safely recommended for temperature determination in similar plasmas.

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