

A Study on Argon Inductively Coupled Plasma with Introduction of Ethanol Solution

I. Effect of Ethanol on Line Intensity of Rare Earth Elements

Yang Jin-Fu(杨金夫), Zeng Xian-Jin(曾宪津)

(Changchun Institute of Applied Chemistry, Academia Sinica, Changchun 130022, China)

Huang Ben-Li(黄本立)

(Department of Chemistry, Xiamen University, Xiamen 361005, China)

Received March 16, 1991

Effect of ethanol on corrected intensity, i.e. the intensity corrected for the rate at which an analyte solution enters ICP, of lines of 10 rare earth elements, Mg, Fe and Cd have been studied. Compared to the aqueous case, the introduction of an ethanol solution results in a decrease in corrected intensity. For all the ionic lines and the atomic lines of Cd, the corrected intensities decrease steadily with increasing ethanol concentration from 0 to 95 vol%, while for the atomic lines of the other elements, the corrected intensities have minima at certain ethanol concentration. For a given element, the higher the excitation energy of a line, the greater the decrease in the corrected intensity with the introduction of ethanol. The depression of corrected intensity by ethanol is linearly related to excitation energy. The above results have been used for identifying the ionization states of 38 lines of rare earth elements and estimating their excitation energies.

Key words: RE, ICP-AES, Line intensity of REE, Ethanol

In our previous publication^[1] on the application of ethanol and desolvation to the analysis of rare earth elements by ICP-AES, an increase in sample introduction efficiency and therefore an improvement in detection limit by a factor of about 10 were reported. However, it was also pointed out that ethanol itself entering ICP depressed line intensity. Ito et al.^[2] and Huang et al.^[3,4] reported that, compared with that in aqueous solution, the introduction of ethanol into an ICP affects both the nebulization of a solution and the excitation characteristics of the plasma and line intensity may therefore change. The purpose of the present work is to study quantitatively the effect of ethanol on line intensity, taking rare earth elements, magnesium, iron and cadmium as representatives. The relationship observed between the effect and the properties of a spectral line was applied to identify the ionization states of some REE lines and estimating their excitation energies.

1. Experimental

A Plasma Therm ICP-5000 source, with a crystal controlled r.f. generator of 40.68 MHz and with automatic power control and impedance matching, was used. The torch is of the Fassel-Scott type. A Meinhard Model TR-30-A3 nebulizer combined with a double-pass spray chamber was used to nebulize solutions. The ICP operated in following conditions, incident power 1.7 kW, observation height 19 mm above load coil, carrier gas rate 0.50 l/min, outer Ar flow rate 18 l/min and intermediate Ar flow rate 1.4 l/min.

A 2-m plane grating spectrograph (Carl Zeiss Jena Model PGS 2) with a 651 groves/mm grating (1st order 0.74 nm/mm), blazed at 320 nm was used to select lines at will.

All solutions were prepared with Specpure or AR grade reagents. The elements, lines and the associated data are listed in Table 1.

Table 1 Elements and their ionization energies (E_i), and lines and their excitation energies (E_q) used in this work

Element	E_i (eV)	λ (nm)	E_q (eV)	Element	E_i (eV)	λ (nm)	E_q (eV)			
Yb	6.22	346.437(I)	3.58	Sm	5.60	447.088(I)	3.05			
		347.631(II)*	3.57			323.964(II)	4.31			
		303.111(II)	4.09	Dy	6.20	421.809(I)	3.60			
		297.056(II)	4.17			343.437(II)				
		345.407(II)	6.90			Gd		6.16	333.213(II)	4.78
		347.884(II)	7.31							
310.789(II)	8.95	Y	6.51	405.393(I)	3.06					
404.763(I)	3.06			422.056(II)	3.80					
374.775(II)*	3.41			Er		331.242(II)				
320.332(II)	3.98						Tm	6.20	371.792(I)	3.33
366.849(II)	6.90			366.808(II)		3.37				
308.686(II)	7.26			Fe		7.87			331.212(I)	3.74
312.993(II)	7.37	296.982(II)	5.63							
301.763(I)	4.22	Lu	6.15		285.213(I)		4.34			
301.898(I)	5.06				280.270(II)		4.42			
303.015(I)	6.52	Mg	7.64		Cd		8.99	228.802(I)	5.41	
301.145(I)	6.87							226.502(II)	5.47	
328.026(I)	7.08									
292.659(II)	5.22									
402.588(II)	3.40									

* The ionic lines of Y and Yb in Figs.1 and 3

2. Results and Discussion

2.1. Some considerations of the factors affecting line intensity

The intensity of a line depends on the characteristics of a source and the concentrations of associated species in the source. Under a local thermal equilibrium (LTE) condition, the intensity I of an ionic line can be expressed by:

$$I = nAh\nu(g/Z)\exp(-E_q/kT) \quad (1)$$

where n is the ion number density, A the transition probability for spontaneous emission, h the Planck's constant, ν the emission frequency, g the statistical weight of the upper level, Z the partition function, E_q the excitation energy, k the Boltzmann's constant and T the LTE temperature. If the secondary ionization of analytes is negligible, the ion number density of an analyte can be derived by:

$$n = \alpha\beta Q_p \quad (2)$$

where α is the ionization degree of an analyte, β a constant related with the evaporation, dissociation and transport of analyte species in plasma, Q_p the rate at which an analyte solution enters ICP. Combination of Eqns (1) and (2) results in

$$I = Q_p \alpha \beta A h \nu (g/Z) \exp(-E_q/kT) \quad (3)$$

Eqn (3) can be simplified as:

$$I = K f Q_p \quad (4)$$

by defining:

$$K = (g/Z) A h \nu \quad (5)$$

$$f = \alpha \beta \exp(-E_q/kT) \quad (6)$$

where K is an optical coefficient determined by the properties of a line, and f is the plasma factor. For an atomic line, an intensity expression as Eqn (4) can also be obtained but α in Eqns (2), (3) and (6) should be replaced by $(1-\alpha)$. It is clear from Eqn (4) that both Q_p and the plasma factor should be considered when the effect of ethanol on line intensity is studied, and that the magnitude of the effect is related to the properties of a line.

2.2. Effect of ethanol on line intensity

A detailed investigation has been made on the effect of ethanol on the intensities of more than 50 REE lines. With 7 atomic lines and 10 ionic lines as representatives (wavelengths and the excitation energies refer to Table 1), the results are given in Fig.1, where the normalized intensity I_N is defined as the ratio of intensities obtained with and without ethanol in the solution. With the increase of ethanol concentration from 0 to 95 vol%, the intensities of all the lines have minima at ethanol concentration of about 10 vol%; and then, the intensity of an atomic line increases rapidly while the intensity of an ionic line increases a little in a somewhat wave-like way. Obviously, the intensity of an atomic line changes with the introduction of ethanol more significantly than that of an ionic line.

We first consider the contribution of changes in Q_p to the effect of ethanol on intensity. Dividing both sides of Eqn (4) by Q_p yields the line intensity corrected for Q_p , I_C :

$$I_C = I / Q_p = K f \quad (7)$$

To obtain the values of corrected intensity I_C , Q_p at different ethanol concentrations was measured. The results along with the solution uptake rate (Q) are shown in Fig.2. It can be seen that Q_p is ever increasing with

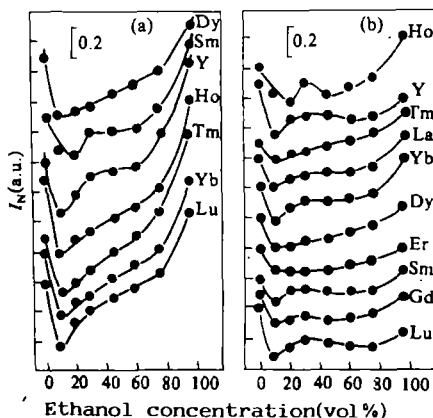


Fig. 1 Effect of ethanol on the normalized intensity (I_N) of atomic lines (a) and ionic lines (b) of rare earth elements

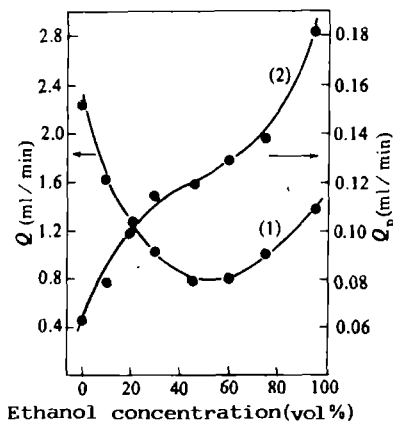


Fig. 2 Effect of ethanol on the uptake rate of solution Q (1) and the rate Q_p ; (2) at which an analyte solution enters ICP

ethanol concentration while Q decreases first, reaches a minimum at about 50 vol% ethanol concentration, and then increases again. Huang et al.^[3-5] reported similar results in their earlier publications. According to Eqn (7) with the intensities shown in Fig.1 and the values of Q_p in Fig.2, the corrected intensities, as given in Fig.3 were calculated. Again, the normalized corrected intensity I_{NC} in Fig.3 is defined as the corrected intensity ratio of lines obtained with and without ethanol in the solution. Clearly, compared to the case of a "pure" aqueous solution, the introduction of ethanol into ICP results in a decrease in corrected intensity for all the lines. However, the changing trend of corrected intensity with ethanol concentration is quite different from an atomic line to an ionic line of a rare earth element: the corrected intensity of an ionic line decreases steadily with increasing ethanol concentration from 0 to 95 vol%, while the corrected intensity of an atomic line has a minimum at about 20 vol% ethanol concentration. This difference may be made use of for identifying the ionization state of a REE line.

As rare earth elements have relatively low ionization energies, further observation was made on the effect of ethanol on some lines of Mg, Fe and Cd (see Table 1). The results show that, for the atomic lines of Mg and Fe and all the ionic lines, the change of corrected intensity with ethanol concentration is similar to that observed for REE lines. Only is the atomic line of Cd exceptional, behaving like an ionic line. This indicates that the effect of ethanol on corrected intensity is related to the ionization energy of an element. We have noticed that the atomic line of Cd and all the ionic lines are "hard" lines and the atomic lines of REEs, Mg and Fe are "soft" lines, as classified by Boumans^[6].

2.3. Relationship between corrected intensity and excitation energy

The Y(II), Yb(II) lines and Fe(I) lines listed in Table 1 were studied to explore the dependence of corrected intensity on excitation energy. The results for Yb(II) lines and Fe(I) lines are shown in Fig.4. For a given element, the higher the excitation energy of a line, the greater decreases in corrected intensity with the introduction of ethanol, and the ethanol concentration corresponding to the minimum I_C of a Fe(I) line is also slightly higher. It can be deduced from the above results that the excitation temperature of the plasma decreases owing to the introduction of ethanol.

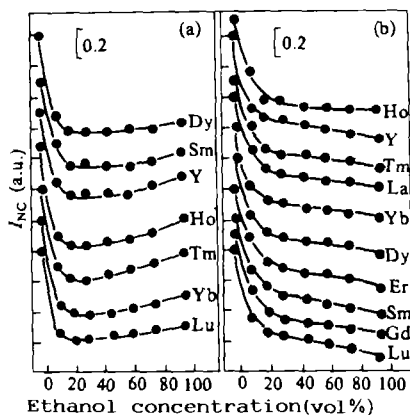


Fig. 3 Effect of ethanol on the normalized corrected intensity (i.e. the intensity corrected for Q_p) I_{NC} of REE lines (a) atomic lines, (b) ionic lines

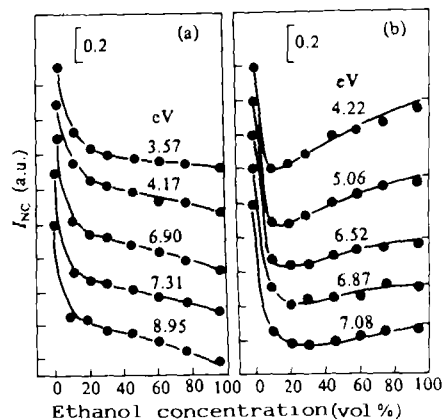


Fig. 4 Effect of ethanol on the normalized corrected intensity I_{NC} of Yb(II) lines (a) and Fe(I) lines (b) with different excitation energies

According to the definition of normalized corrected intensity I_{NC} and Eqns (6) and (7), we have:

$$I_{NC} = \frac{(I_C)_{et}}{(I_C)_{aq}} = \frac{(\alpha\beta)_{et}}{(\alpha\beta)_{aq}} \exp\left[-\frac{E_q}{k} \left(\frac{1}{T_{et}} - \frac{1}{T_{aq}}\right)\right] \quad (8)$$

where the foot-notes of "et" and "aq" refer to ethanol solution and aqueous solution, respectively. By expanding Eqn (8) in a power series and neglecting the terms with n -th ($n > 2$) power in the series, a linear correlation between I_{NC} and E_q is then obtained:

$$I_{NC} = \frac{(\alpha\beta)_{et}}{(\alpha\beta)_{aq}} \left[1 - \frac{1}{k} \left(\frac{1}{T_{et}} - \frac{1}{T_{aq}} \right) E_q \right] \quad (9)$$

Equation (9) can be simplified as:

$$I_{NC} = a - bE_q \quad (10)$$

by definitions:

$$a = \frac{(\alpha\beta)_{et}}{(\alpha\beta)_{aq}} \quad \text{and} \quad b = -\frac{a}{k} \left(\frac{1}{T_{et}} - \frac{1}{T_{aq}} \right)$$

For atomic lines, a similar relationship was also derived. Fig.5 shows some experimental results obtained at a ethanol concentration of 95 vol%. The correlation coefficients of the linear regression plots for Y(II), Yb(II) and Fe(I) lines are 0.93, 0.997 and 0.999, respectively. At the confidence level of 95%, the regression plots for Y(II) and Yb(II) lines are statistically the same. The weighted averages of the regression coefficients a and b are 0.628 and 0.0661, respectively. Putting the values into Eqn (10) and making some rearrangement, we then have:

$$E_q = 9.50 - 15.13 I_{NC} \quad (11)$$

With Eqn (11), the excitation energies of the ionic lines of the REEs in Table 1 (except Y and Yb) were calculated. As shown in Table 2, the deviations of the calculated values from the true values are within $\pm 10\%$. The result implies that all ionic lines of REEs may follow the same relationship between I_{NC} and E_q and Eqn (11) may be made use of for estimating the excitation energy of an ionic line of a REE.

Table 2 Excitation energies (E_q) of some ionic lines of rare earth elements: true and calculated values

Element	λ (nm)	E_q (eV)		Relative error (%)
		Calculated	True	
La	402.588(II)	3.52	3.40	+3.5
Sm	323.964(II)	3.98	4.31	-7.7
Gd	333.213(II)	4.39	4.78	-8.2
Dy	343.437(II)	3.81	3.60	+7.2
Tm	366.808(II)	3.27	3.37	-3.3
Ho	422.056(II)	3.18		
Er	331.242(II)	4.18	3.80	+10
Lu	296.982(II)	5.25	5.63	-6.7

2.4. Identification of ionization state and estimation of excitation energy

There are quite a few of REE lines whose ionization states and excitation energies are still unknown^[7,8].

Such 38 lines were identified to be ionic lines according to the effect of ethanol on their corrected intensity. The excitation energies were also estimated with Eqn (11). The results are given in Table 3.

3. Conclusion

Effect of ethanol on the line intensity corrected for the rate at which an analyte solution enters ICP (briefly, corrected intensity I_C) has been studied in some detail. The introduction of ethanol into ICP depresses the corrected intensity and the magnitude of the depression is linearly related to excitation energy. The changing trend of the corrected intensity with ethanol concentration depends on both the ionization state of a line and the ionization energy of an element. For rare earth elements, the corrected intensity of an ionic line is ever decreasing with increasing ethanol concentration from 0 to 95 vol% while the corrected intensity of an atomic line has a minimum at about 20 vol% ethanol concentration.

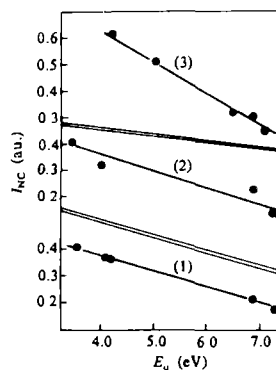


Fig. 5 Dependence of normalized corrected intensity I_{NC} on excitation energy obtained at 95 vol% ethanol concentration
(1) Yb ionic lines; (2) Y ionic lines;
(3) Fe atomic lines

Table 3 Identification of the ionization states (IS) and estimation of the excitation energies of REE lines

Element	λ (nm)	IS	E_q (eV)	Element	λ (nm)	IS	E_q (eV)
Ho	308.436	II	4.22	Tm	323.151	II	4.25
	311.850	II	4.46		324.586	II	2.89
	320.176	II	5.13		325.134	II	6.17
	323.690	II	2.96		325.164	II	4.40
	323.740	II	3.46		326.410	II	3.39
					330.693	II	4.37
Gd	300.357	II	5.23	Tb	295.621	II	4.55
	301.220	II	4.98		302.029	II	4.82
	302.898	II	4.75		302.733	II	3.86
	304.034	II	5.07		303.160	II	4.14
	305.357	II	4.67		318.725	II	2.95
	326.823	II	3.10	Er	296.876	II	3.07
	328.158	II	4.67		303.131	II	3.74
328.225	II	4.33	327.770		II	3.46	
			327.822		II	3.72	
Dy	302.616	II	3.15	327.933	II	4.25	
	303.829	II	4.79	328.618	II	3.36	
	310.975	II	4.81	330.558	II	4.13	
	334.100	II	4.99	373.817	II	3.72	
	341.963	II	4.31				
	343.932	II	4.63				

References

- [1] Yang Jinfu, Huang benli and Pei Aili, Fenxi Huaxue(in Chin.), 1988, 16, 198.
- [2] T. Ito, H. Kawaguchi, A. Mizuike, Bunseki Kagaku, 1978, 28, 648.
- [3] Wang Xiaoru, Huang Benli, Sun Yaru, Liu Chunlan, Fenxi Huaxue(in Chin.), 1983, 11, 1.
- [4] Huang Benli, Spectrochim. Acta, 1983, 38B, 81.
- [5] Huang Benli, Pei Aili, Wang Chuendeh, Acta Physica Sinica(in Chin.), 1966, 22, 733.
- [6] P.W.J.M. Boumans, Invited lecture presented at the 25th Canadian Spectroscopy Symposium, Mont Cabriel, September, 1978, 1.
- [7] J. A. Norris, "Wavelength Table of Rare Earth Elements and Associated Elements Including Zirconium, Thorium, Hafnium, Rhenium and Tellurium". Publication of ORNL-2774, Oak Ridge National Laboratory operated by Union Carbide Corporation for the U.S. Atomic Energy Commission, 1.
- [8] Massachusetts Institute of Technology, "Wavelength Tables", Cambridge, Massachusetts and London, England, The M.I.T. Press, 1969, 1.

* * * * *

The 2nd Chinese–Soviet Conference on Chemistry and Application of Rare Earths Held in Changchun and Shanghai

The 2nd Chinese–Soviet Conference on Chemistry and Application Rare Earths was held at Changchun Institute of Applied Chemistry, Academia Sinica, and Shanghai Institute of Metallurgy, Academia Sinica, China, on October 5~ 11, 1991. 10 representatives from USSR attended the conference. There were 47 Chinese representatives in Changchun Conference and 77 in Shanghai Conference respectively. Prof. Ni jiazan, Chinese chief representative, gave a lecture entitled "Progress and Research on Rare Earth Chemistry in China". and Prof. I.A. Smirnov gave another lecture entitled "Physico–Chemical Investigation and Perspective of Practical Application of CeO_2 – PrO_2 ".

99 papers were contributed to the conference, among them 24 papers were presented in Changchun Conference and 21 papers in Shanghai Conference, and the rest were posted during the conference. All the papers are collected in the proceedings (in English). The papers are concerned with RE chemistry, RE separation and extraction, RE element analysis, RE applications in superconductors, luminescence materials and magnetic materials, etc.

The 1st Chinese–Soviet Conference on Chemistry and Application of Rare Earths was held in USSR in 1989, and the 3rd one will also be held in USSR in 1993.