Indian J. Phys. **52B**, 167–172 (1978)

Stability of intensity ratio of line pairs

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(*Received* 25 *March* 1976)

In spectrochemical analysis, frequently, elements sought are required to be determined in a wide variety of compositional types. Often a question arises concerning the stability of the intensity ratio of the analysis-internal standard line pair in regard to such changes.

The present paper explains the behaviour of the intensity ratio with variation of temperature, electron pressure and degree of ionization for both ideal and unideal internal standard.

1. INTRODUCTION

Selection of the internal standard yields to certain specification according to Ahrens & Taylor (1961). Of the most important, is that the excitation characteristics of either the analysis or internal standard elements are similar. Yet, applying such a restricted requirement in spectrochemical analysis is often met with obstacles. As an example, the absence of an internal standard with similar excitation characteristics to the analysis element. On the other hand, Boumans (1966) suggested, the dropping of such regorous demand. He only claimed that the function of the internal standard in mainly to meet irregularities in the evaporation and plate errors.

In fact selection of a satisfactory internal standard necessitates the fulfilment of two major factors, its volatilization beside its behaviour in the plasma. The internal standard should vaporize in a similar manner to the analysis element. Meanwhile, the internal standard should eliminate the influence of variation of the excitation conditions. Practice has shown that volatilization characteristics is usually much more important than excitation characteristics.

In this paper the intensity ratio of line pair against the variation of temperature, electron pressure and degree of ionization has been studied for two groups of line pair. The first line pair group, have similar volatilization and excitation characteristics. The second group have different volatilization and excitation characteristics.

A. *Line pair with similar volatilization and excitation characteristics.*

In this study two pairs were selected, one pair copper/lead represents volatile elements while another represents the involatiles. The wavelength, the excita-

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tion potential of the four spectral lines beside the ionization potential of the four elements are given in table 1.

Table 1. Excitation and ionization potential of the selected elements

Group	Elements	Ionization potential	Wavelength	Excitation potential
Volatiles	Cu (analysis line)	7·72 eV	3273·96 Å	3·77 eV
	Pb (reference line)	7·42 eV	2833·07 Å	4·40 eV
Involatiles	Co (analysis line)	7·86 eV	3044·01 Å	4·07 eV
	Ni (reference line)	7·63 eV	3444·77 Å	3·65 eV

The behaviour of the intensity ratio of the selected spectral lines with temperature and electron pressure resulting from studied matrices is illustrated in figures (1) and (2).

The effect of the degree of ionization is explained as follows, it is well known that with different matrices, change of arc temperature occurs. It is well known that the degree of ionization of any element varies in accordance with Saha's relationship. Suppose now an internal standard element has a low ionization potential, whereas that of the analysis element is high. Naturally, a change in the source temperature alters the degree of ionization for both elements in the same direction, but not to the same extent. Consequently, the intensity ratio of the analysis pair will vary with different temperatures.

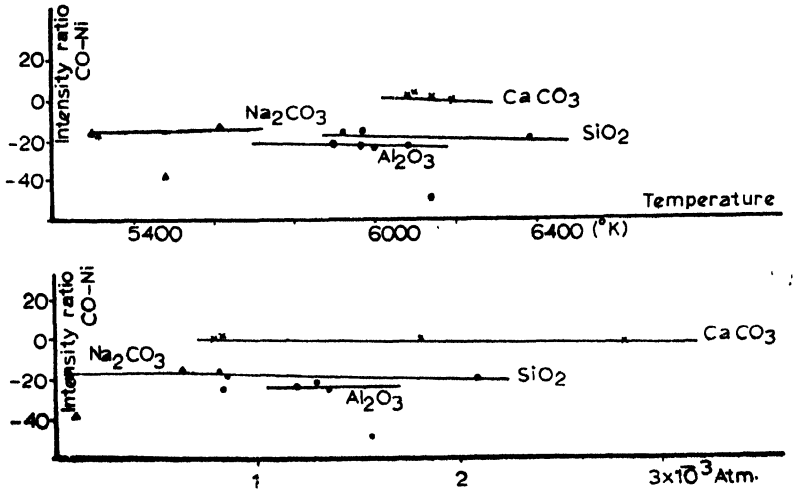

Fig. 1

In this work the ionization potential of copper resembles that of lead. Also cobalt has nearly the same value as for nickel. Fortunately, the degree of

ionization of both copper, lead and cobalt, nickel have been previously calculated for the different matrices.

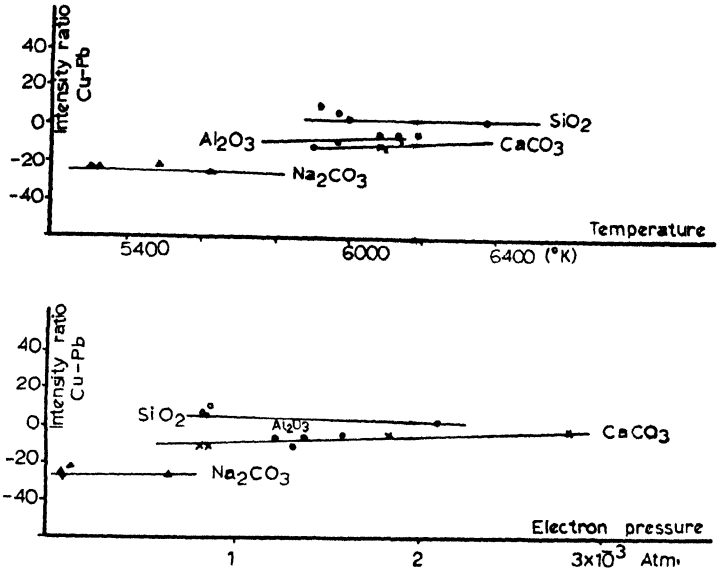

Fig 2

It is clear from the achieved results, that the respond of ionization of each analysis element resembles the respond due to the internal standard. Consequently any variation in the analysis line intensity due to ionization, will be eliminated due to equal variation in the internal standard line intensity.

In this work from figures (1) and (2), it is obvious that the intensity ratio of analysis-internal standard line pair with different temperature and electron pressure produced from studied matrices is stable. The stability occurs for either copper/lead or for cobalt/nickel pair.

Naturally, this behaviour was expected since the selected reference line of each pair is an ideal internal standard. Langstroth & Andrychuck (1948) observed also small variation for line pairs having nearly equal excitation potential. Also Scott (1945) indicated that the response of such lines to change of matrix is very similar.

B. *Line pair with different volatilization and excitation characteristics*

In this study, gallium was chosen as internal standard for all volatile elements. Also ytrium was selected as internal standard for involatile elements. The specifications of studied elements of both volatiles and involatiles are given in table 2.

Table 2. Specifications of studied elements

Group	Element	Ionization potential	Wavelength	Excitation potential
Volatiles	Ca (I.S.)	5·97 eV	2874·24 Å	4·30 eV
	Pb	7·43	2833·07	4·40
	Ag	7·58	3280·68	3·75
	Cu	7·72	3273·96	3·77
	As	10·50	2349·84	6·60
Involatiles	Y (I.S.)	6·50 eV	3203·00 Å	-
	Zr	6·95	2571·39	—
	Mo	7·06	2816·15	—
	Ni	7·63	3414·77	3·65 eV
	Co	7·86	3044·01	4·07

The manner by which the intensity ratio of selected spectral lines with temperature and electron pressure resulting from studied matrices are illustrated in figures (3) and (4).

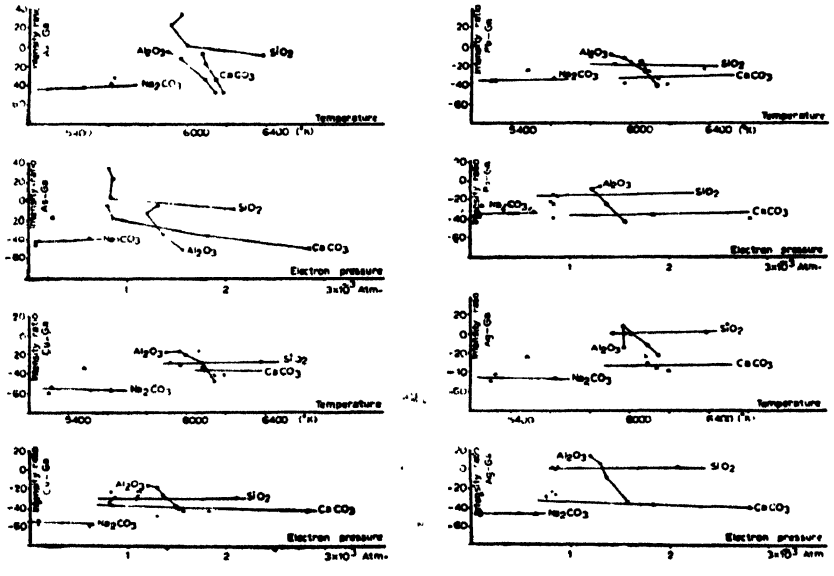

Fig. 3

In this group and from previous conclusion in paper III, the degree of ionization of most elements (either volatiles or involatiles) has a small or negligible effect with regard to variation in line intensity. Normally this behaviour was expected due to the limited range of both temperature (5400–6400°K) and electron

pressure ($1-3\times10^{-3}$ atm) yielded by studied matrices. Consequently the influence of degree of ionization on intensity ratio of line pairs will not be further discussed.

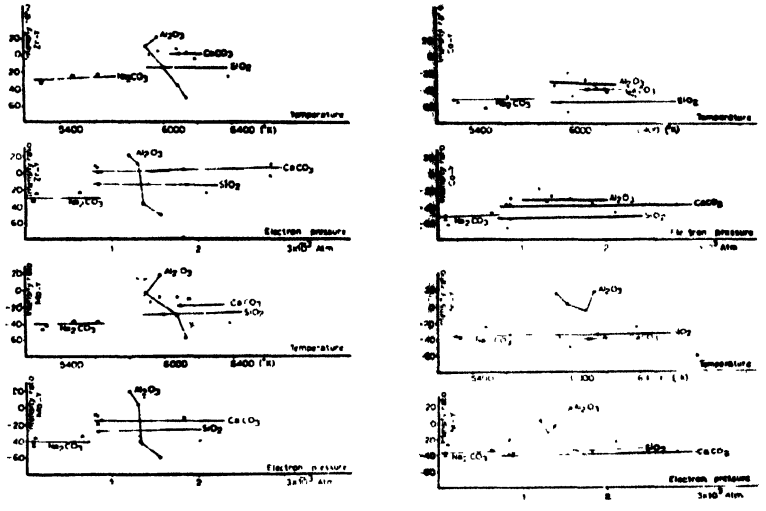

Fig. 4

In this part either gallium or yettrium does not represent an ideal internal standard for either volatile or involatile elements. The reason is simply because each of them does not possess the specifications of the proper internal standard for his group (table 2). Hence several factors has to be considered. The much more important is the way of burning of the arc.

Naturally, a smooth burning discharge, reduces or eliminates marked difference in volatilization of both analysis and internal standard lines. Consequently, the intensity ratio is relatively stable with different temperatures. On the contrary, with an erratic discharge, there is always a great probability that uncontrolled loss of material could occur in the evaporation process. Hence the intensity of the analysis element would vary from that of the internal standard. Consequently, the resultant intensity ratio is unstable.

In routine spectrochemical analysis, it is always desirable to use a single internal standard to serve for the analysis of several elements. With a smooth burning, this request could be satisfactorily applied. As the discharge becomes erratic, a separate internal standard may have to be used for each element, or at least for a very limited number of elements.

From figures (1) and (2), it is clear that the intensity ratio of the studied line pairs volatiles (Ag/Ga, As/Ga, Cu/Ga and Pb/Ga) and involatiles (Co/Y,

Ni/Y, Mo/Y and Zr/Y) are relatively stable in sodium carbonate matrix. Similar conclusion was previously obtained by Longstroth and Newbound 1942. Although the studied pairs represent diverse values of excitation and ionization potential, yet this result was expected because of the smooth burning exerted by sodium carbonate matrix

Consequently, one can decide that with great certainity, employing sodium carbonate matrix, gallium could be used as an internal standard for volatile elements. Also the same principle could be applied for yttrium with respect to involatiles.

The matrices calcium carbonate and silicon dioxide afford small or negligible variation in the intensity ratio of certain pairs (volatiles Ag/Ga, Cu/Ga and Pb/Ga) and involatiles (Co/Y and Ni/Y). It is clear that the cause is the similarity in excitation characteristics between each element and its internal standard.

Aluminium oxide, is the only matrix that affords unstable intensity ratios for all line pairs Needless to explain that the main cause to this phenomena is that with the increase of aluminium concentration, a great probability of the formation of residual bead or globule exists Hence loss of the formed alumina bead out of the electrode cavity during burning could occur.

References

Ahrens H. & Taylor 1961 *Spectrochemical Analysis* 2nd ed. Addison Wesley.

Boumans P. W. S. M. 1966 *Theory of Spectrochemical Excitation*, Hilger & Watts Ltd., London.

Longstroth G. O. & Andryshuck D. 1948 *Can. J. Research* **26A**. No 2, 39 49.

Scott R. O. 1945 *J Soc. Chem. Ind.* **64**, 189.

Longstroth G O. & Newbound K. B. 1942 *Can. J. Research*, **20A**, 39-47.