CURVE OF GROWTH METHODOLOGY APPLIED TO COPPER RESONANCE LINES AT 324.7, AND 327.4 NM BY ATOMIC ABSORPTION MEASUREMENTS

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Abstract

The curves of growth (*COGs*) of two copper resonance lines, having excited levels $4p\ ^2P^0_{3/2}$, and $4p\ ^2P^0_{1/2}$ with wavelengths *324.7*, and *327.4 nm* respectively, emitted from copper hollow-cathode lamp have been investigated on the basis of atomic absorption spectroscopy. The experimental curves of growth were obtained by measuring the Absorbance, $A = \log\frac{I_o}{I}$ for each line for a wide range of concentrations (*1-1000ppm*). The total absorption A_t is calculated for Lorentz spectral line shapes. Graphical plots of the optical depth τ with the number density of free atoms in the ground $N(cm^{-3})$ are also provided. The results obtained have been compared with those previously reported.

Keywords: Curve of growth, Absorbance, Optical depth, Total absorption.

1. Introduction

Conventional atomic absorption spectroscopy (*CAAS*) still provides a good technique for accurate elemental analysis with several advantages over emission spectroscopy. It is, in general, a more frequently used technique in all regions of the spectrum. One of the most frequently used concepts in atomic absorption spectrometry is that of an easily measurable quantity called Absorbance A. Whenever Beer's law is valid, the absorbance A is linear with the concentration of the analyte over a large range of concentrations. It is also fairly straightforward to work with since A consists of base *10* logarithm of the ratio of two quantities that are easily measurable in *CAAS*: the intensities in the absence and in the presence of the analyte, I_0 and I, respectively. The double logarithmic plot of $A = \log\frac{I_o}{I}$ against $\log C$ constitutes the so called experimental curve of growth (*COG*). The concept of the *COG* in emission spectroscopy was first experimentally investigated

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in pioneering works by Ladenburg and Reiche in 1910 and then developed in detail by Mitchell and Zemansky, and many others[1]. The *COG* method was further developed for flame spectroscopy by Hinnov[2] and Alkemade et al [3]. One of the most interesting application of the method of *COG* in the field of astrophysics is the determination of stellar temperature and the elemental abundances. Lastly the COG concept is applied to the laser-induced plasma in order to obtain useful information on several fundamental plasma parameters[4].

However, the absorption spectrum has several disadvantages such as line broadening, and self-absorption. In particular, self-absorption of the most intense lines (e.g. resonance lines) is a critical problem, as it produces a much lower measured intensities than theoretical predictions. The severity of self-absorption varies with the optical depth of the spectral line. The optical depth depends on the number density of absorbing atoms in the ground state responsible for absorption, which in turn is related to the concentration of the element in the sample. The optical depth is also a function of the line profile, and the atomic transition parameters through the oscillator strength of the emission line considered [5].

The main idea of this paper is to apply the *COG* methodology for flame spectroscopy in order to obtain valuable information, such as spectral line behavior, and to estimate fundamental parameters such as atom number densities responsible for the absorption process. Atomic absorption measurements on the copper resonance lines at *324.7*, and *327.4nm* are analyzed. The Absorbance A is measured assuming a Doppler and Lorentz line profiles for the source and the flame at *2400°K* respectively. The Absorbance A varies with the optical depth τ, and hence with the number density of absorbing atoms in the ground states, $N(m^{-3})$. Since it is important to describe the saturation of the line intensities due to self-absorption, the optical depth τ is determined for a wide range of concentrations for Lorentz line profile.

2. Theoretical consideration

Some common ways to write Beer's law, in exponential form are as:

$$I = I_0 e^{-k\ell C} \tag{1}$$

Where k is the absorption coefficient, ℓ the length of the interaction region (or absorption path length), and C the concentration of the analyte (all expressed in suitable units that make the exponent dimensionless).

Absorbance is defined as the logarithmic of the ratio of the intensities in the absence and in the presence of absorbers I_0 and I respectively.

$$A = \log \frac{I_0}{I} \tag{2}$$

We will refer to Absorbance A as given by the above equation (2) as the observed absorbance [6].

The optical depth $\tau(\upsilon)$ of the spectral line is related to the absorption coefficient k by:

$$\tau(\upsilon) = \int_0^{\ell} k d\ell \tag{3}$$

For homogeneous plasma in local thermodynamic equilibrium (LTE), equation (3) becomes; $\tau(\upsilon) = k\ell$.

In the case of visible and *UV*, absorption lines $h\upsilon >> kT$, the lines are therefore formed in the pure absorption case, and the stimulated emission is unimportant. Under these conditions, we may write the optical depth in the following form [7]:

$$\tau(\upsilon) = \frac{e^2}{4\varepsilon_0 mc} Nf\ell P(\upsilon) \tag{4}$$

With, e, ε_0 m, and c have their usual meaning. N is the number density of absorbing atoms in the ground state, $P(\upsilon)$ is the normalized line profile, and f is the electronic oscillator strength it is given as:

$$f = \frac{g_u}{g_l} \frac{\varepsilon_0 mc}{2\pi e^{2^2}} \lambda^2 a_{ij} \tag{5}$$

With the transition probability a_{ij} in s^{-1}, g's are the statistical weights of the upper and lower levels respectively.

When the line is broadened by collisions of neighboring identical atoms, this leads to a Lorentzian line profile of the form:

$$P(\upsilon) = \frac{1}{\pi} \frac{\Delta\upsilon_L}{(\Delta\upsilon_L)^2 + (\Delta\upsilon)^2} \tag{6}$$

the optical depth for Lorentz line profile in terms of the wavelength becomes [8]:

$$\tau^L(\lambda) = \frac{e^2}{4\pi\varepsilon_0 mc^2} Nf\ell \frac{\lambda^2 \Delta\lambda_L}{\Delta\lambda_L^2 + \Delta\lambda^2} \tag{7}$$

With $\Delta\lambda_L$ is the Lorentz half-width.

The integrated intensity of a spectral line emitted by an optically thick plasma (Wm^{-2}sr^{-1}) is given by [9]:

$$I = I_P(\upsilon_0) \int (1 - e^{-\int_0^{\ell} k(\upsilon,x) d\ell}) d\upsilon \tag{8}$$

Where υ_0 is the central frequency of the transition (s^{-1}), $I_P(\upsilon_0)$ is the Planck distribution for black-body radiation (Wm^{-2}sr^{-1}Hz^{-1}), and $k(\upsilon, x)$ is the frequency-dependent absorption coefficient (m^{-1}), for a homogeneous flame or plasma the absorption coefficient is independent of the path length, and the integration in the exponent is replaced by $k(\upsilon)\ell$.

The spectral line intensity introduced by the equation (8) can also be rewritten in terms of total absorption A_t multiplied by a proportionality constant. The total absorption is defined as [see ref. 1] :

$$A_t = \frac{2\pi}{\sqrt{\ln 2}} \frac{c\Delta\lambda_D}{\lambda^2} \int_0^\infty \left(1 - e^{-k(\lambda)\ell}\right) d\lambda \qquad (9)$$

From equation (9) it is clear that A_t is related to the optical depth $\tau(\upsilon)$, and consequently with the number density of absorbing atoms in the ground state $N\ (m^{-3})$. Therefore, we may calculate A_t once the optical depth $\tau(\upsilon)$ is calculated for Doppler, Lorentz, and Voigt line profiles.

The numerical estimation of the number density $N\ (m^{-3})$ of free atoms in the ground state responsible for absorption, can be estimated from a given experimental conditions. The details of the experimental studies are found in reference [10]. In analytical atomic absorption spectroscopy, instead of the integrated absorption, the peak absorbance is measured. In the case of narrow line source of Gaussian profile, (i.e. assuming a Doppler profile for the source line), and assuming a SI system of units, the expression for the peak absorbance A_p [11]:

$$A_p = 3.83 \times 10^{-15} \frac{\lambda^2}{\Delta\lambda_D} Nf\ell \qquad (10)$$

Substituting by numerical values of f, λ, $\Delta\lambda_D$, and ℓ in equation (10), values of N (m^{-3}) could be estimated.

3.Measurements

The Atomic absorption spectrometer (Perkin-Elmar 2380) with long rectangular 10 cm burner was used. An aqueous salt solutions with different concentrations ranging from 1to 1000ppm were prepared for Cu. The solutions were sprayed into an air/acetylene flame at a temperature of about 2800°K. The acetylene flow rates were fixed at constant pressure to give the maximum values of absorbance for different concentrations. The optical depth and the number density of the absorbing atoms in the ground state, were calculated for each concentration using equations (7) and (10) respectively [12].

4. Results, discussion, and conclusions

The experimental results relating the measured observed Absorbance A_{obs} to the concentration *C(ppm)* for the two *Cu* resonance lines at *324.7, 327.4nm* are presented in Fig 1, and Fig 2. As can be seen, the measured absorbance increases rapidly at first, and then undergoes much less variations at high concentrations. According to Fig. 1, the departure from linearity occurs at a concentration of

100ppm for the line at *324,7nm*, and occurs at *130ppm* for the line *327.4nm*. Thus, we find the expected result that Beer-Lambert law does not hold for large concentration. It is also found that A_{obs} for the resonance line *324.7nm* is greater than that for the line *327.4nm* at the same concentration. The sensitivity ratio, which is defined as the ratio of the observed Absorbance of the two lines at the same concentration is greater for the line *324.7nm*. This is shown in Fig 3, which gives the sensitivity ratio of the two lines as a function of concentration. We may therefore conclude that the resonance line at *324.7nm* should be used in atomic absorption investigations of copper since it has an average sensitivity approximately *1.713* times greater than the *327.4nm* line. It is evident that the *324.7nm* line is more strongly subject to self-absorption.

Fig. 4 shows the theoretical COG for the *Cu* resonance lines at *324.7, 327.4nm*. The theoretical COG has been calculated using Fortran Power Station software and a polynomial approximation of the integrals in equation (10). The theoretical COG must have two asymptotes with slopes *1*at low concentration, and ½ as the concentration increases. to contain valuable information on several fundamental plasma parameters. It was found for example that the damping constant is equal to *0.809* for the copper resonance line at *324.7 nm*, and *0.538nm* for the line *327.4nm*. These values are in good agreement with the values determined by the relevant methods such as in the case of Li [13].

The optical depth of spectral lines has important consequences in the different CAAS. Fig 5 depicts the relation between the optical depth assuming Lorentz line profile against the number density of absorbing atoms in the ground state, for the two copper resonance lines at *324.7 nm*, and *327.4nm*.

The first line shows a linear relation with the number density, while the second line gives different shape. CAAS plasmas generally present a low density of atoms. As a consequence, the absorption of spectral lines is often characterized by a low optical depth due to the self-absorption of the absorbed radiation. The optical depth and the corresponding saturation of the line intensities are determined by two main factors in a given experiment. Firstly, for a certain absorption line, the optical depth depends on the density of the absorbing species present, which is related to the concentration of the element. Secondly, the optical depth depends on the absorption line considered. In a simple description, intense lines are more saturated than weak lines.

5. Conclusion

From the results obtained we may conclude that the curves of growth method applied to conventional atomic absorption spectroscopy is a valuable method for obtaining several plasma parameters, such as damping constant atom number densities in the ground state responsible for absorption, and optical cross-sections. Self-absorption by unexcited atoms is the dominant mechanism for reducing the applicability of Beer's law, and therefore produces a critical problem. It will have the effect of broadening a spectral line and will, therefore, produce an apparent width which is too large. The severity of self-absorption varies with the optical depth. If the optical depth is not large ($\tau < 1$), one may correct the measured absorbance to the limit of an optically thin layer.

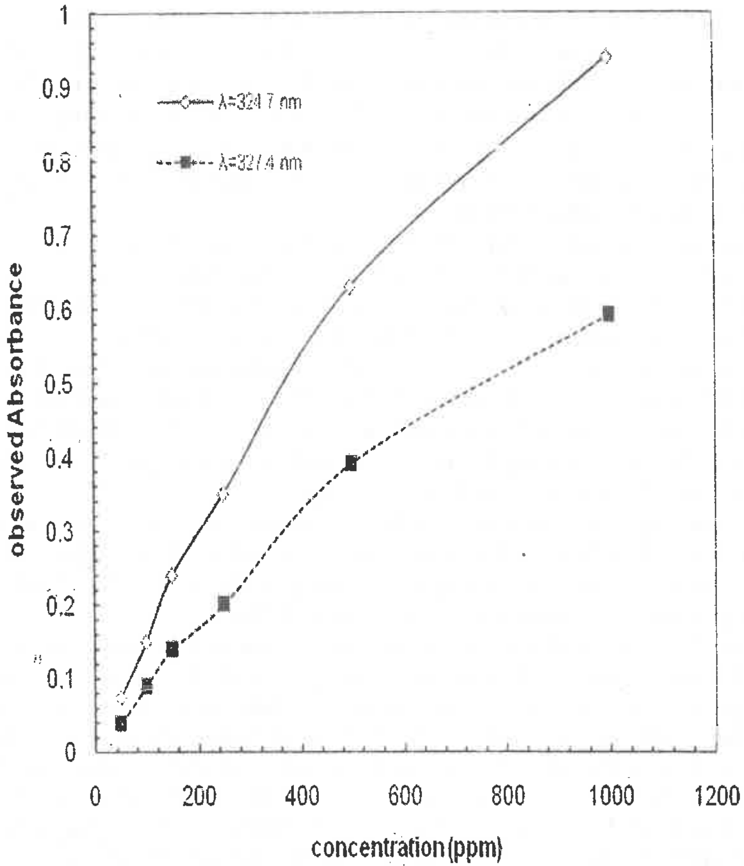

Fig 1. The experimental COG for the copper resonance lines at 324.7 & 327.4 nm with a linear scale

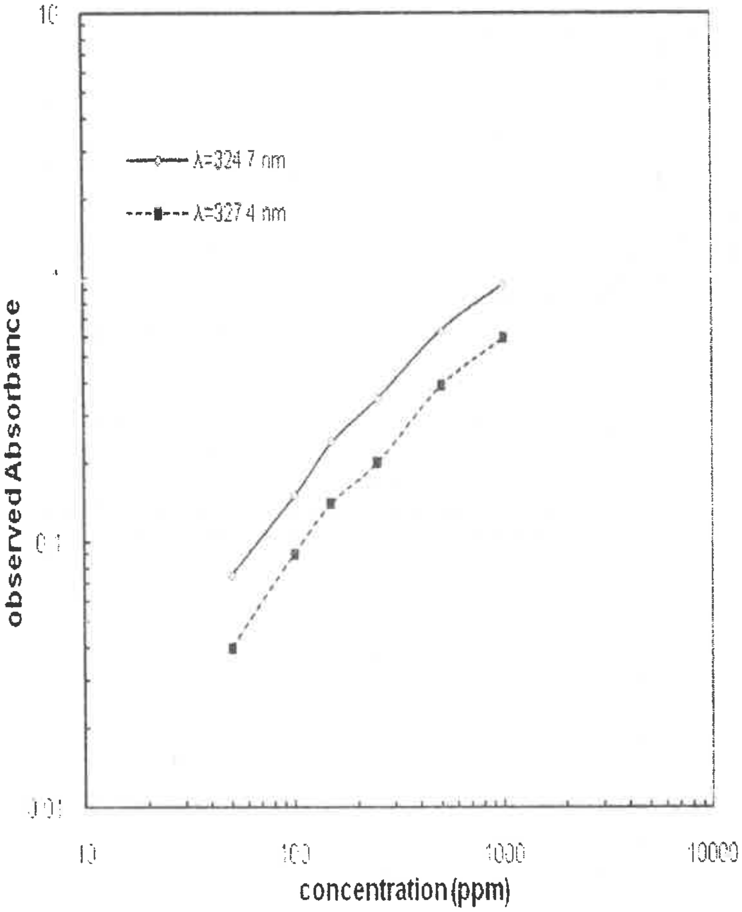

Fig 2. The same as Fig1 on double logarethmic scale

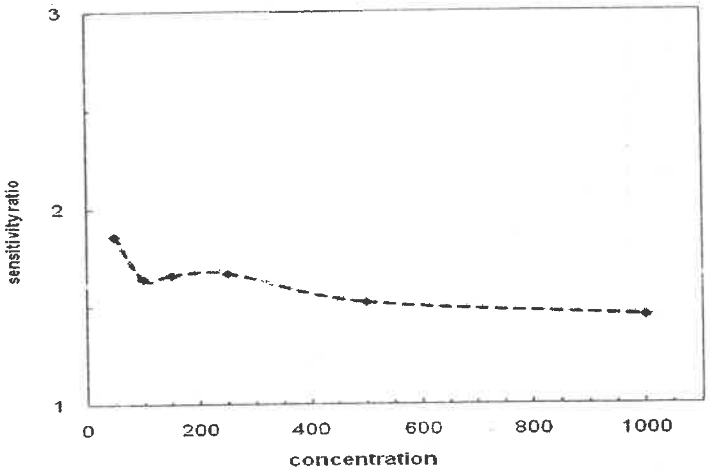

Fig 3. The sensitivity ratio for the two copper lines as a function of concentration C(ppm)

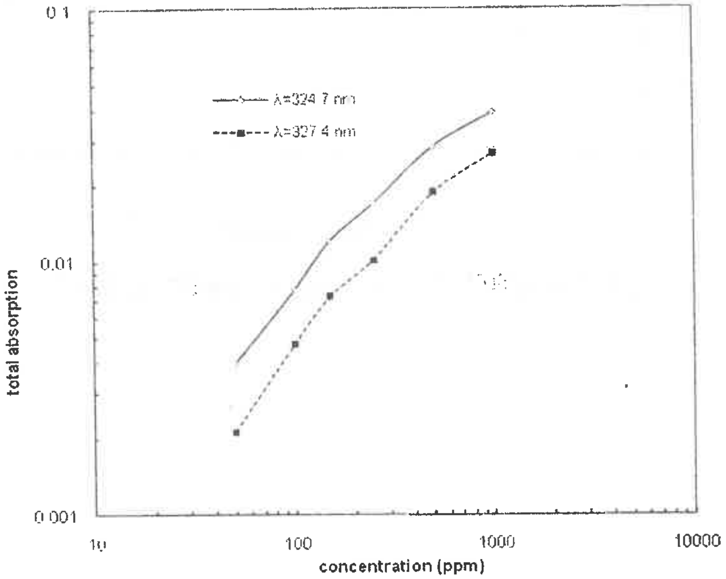

Fig4. Theoretical COGs for copper resonance lines at 324.7 & 327.4 nm with double logarithmic scale

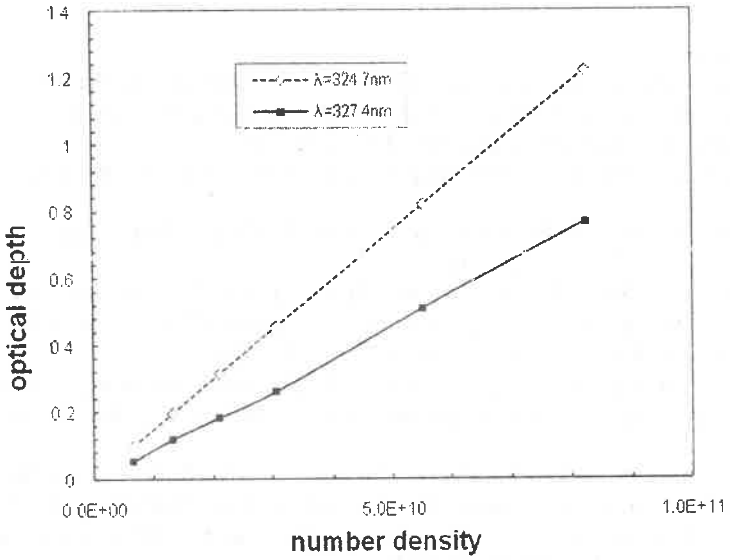

Fig 5. The optical depth of copper resonance lines at 324.7 and 327.4nm as a function of N(cm-3)

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