

## **THE EFFECT OF SELF-ABSORPTION ON THE DETERMINATION OF NICKEL BY FLAME ATOMIC ABSORPTION SPECTROMETRY**

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### **ABSTRACT**

Nickel was determined by the conventional flame atomic absorption spectrometry (FAAS) at the upper trace range. The absorbance was measured for a wide range of concentration (10-100 mgL<sup>-1</sup>) at the resonance lines 232.0 and 352.34 nm for nickel. Using ordinary least square fitting, the calibration curve corresponding to the measured absorbance with the corresponding concentration was constructed for each line. Based on straight line regression, the measurements were validated by calculating the limit of detection (LOD) for the two nickel lines under investigation. The effect of self-absorption on the measured absorbance was studied. A simple method was developed in order to estimate quantitatively the self-absorption effects for the resonance lines of nickel by means of the escape factor. The reliability of the escape factor method was verified by providing calibration curves of some environmental elements Na, Ca, Cd and Zn. The results obtained for the limit of detection (LOD) for the elements under consideration were compared with those found in literature.

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Kew words: Nickel; Absorbance; Self-absorption; Limit of detection

## **1. INTRODUCTION**

Nickel is a natural element which is found abundantly in our atmosphere from power plants using oil and coal burning as well as many other industrial resources and waste materials. Nickel typically occurs in crude oil in the upper trace range 2 – 200 mgL<sup>-1</sup>. Nickel compounds can enter water from dissolution of rocks, soils and biological cycles. On the other hand, the concentration of nickel in natural water and some real food samples is generally at the lower trace range. The standard level of nickel for drinking water is 0.1 mgL<sup>-1</sup> [1,2]. According to the international regulation on water quality, the approved content of nickel in drinking water is 0.02 mgL<sup>-1</sup>. Compared with other transition metals, nickel is less toxic element. However, the trace amount of nickel is indicated to be either essential or toxic depending on its concentration range. In addition, both excess and deficiency of certain nickel compounds may be carcinogenic [3,4]. For these reasons it is important from an analytical point of view to develop accurate and economical methods for determination of nickel amounts in a wide range of samples for a wide range of concentrations.

Among a great variety of potential analytical techniques (e.g. inductively coupled plasma mass spectrometry (ICP-MS) and Laser-induced plasma spectroscopy (LIPS)), conventional flame atomic absorption spectrometry (FAAS) still provides a flexible experimental set-up for quantitative determination of trace metals. FAAS was introduced to the world of analytical chemistry by Walsh in 1955 [5]. Since then, the technique was welcomed by analytical chemists as a powerful method for trace elements analysis. The reason for the usefulness and the popularity of FAAS is that it rely upon separate measurements of the intensities in the absence and in the presence of the sample which are needed for the determination of absorbance. The absorbance expresses an easily measurable quantity that is linear with the concentration of free atoms in the beam path responsible of absorption whenever Beer – Lambert law is valid. The double logarithmic plot of measured absorbance with concentration constructs the so called experimental curve of growth (COG) from which the Voigt a-parameter could be determined under experimental conditions. The Voigt a-parameter is of great importance since it yields an important

information about collision (Lorentz) against Gaussian (Doppler) line broadening [6]. FAAS available in most laboratories relatively simple, inexpensive, and usually less subject to interference than other spectroscopic methods. Compared to other potential available methods for the trace elements determination, FAAS is a direct method that does not require sample preparation. For these reasons flame atomic absorption spectroscopy is considered universal technique for the determination of trace metals in a wide range of samples. Classification, historical evolution and ways to improve the sensitivity of FAAS were reviewed by Ataman [7].

In order to achieve accurate and sensitive results at lower trace levels of nickel, various methods based on pre-concentration and separation were established [8 – 12]. There are several reasons why the extraction techniques are very suitable subjects for good analytical performance. Also, they provide results comparable to those obtained with other separation methods. However, several inconveniences reduce the applicability of these techniques. The chemical variables affecting the separation phase and the viscosity [13] affecting the detection process cannot be overcome. On the other hand, the absorption in FAAS is mainly determined by the density of the ground state neutral atoms which is proportional to the concentration of the element. Consequently, at higher absorbance values a deviation from Beer-Lambert law is frequently observed in practice for emission lines where the lower level of transition is equal to or near to the ground state. This deviation can be seen as a curvature of the calibration curve (absorbance versus concentration) towards the concentration axis. Unfailing calibration still remains a significant problem from the experimental point of view [14].

Self-absorption of a spectral line reduces the absorbance of than expected thus causes non-linearity of the calibration curve. If the phenomenon of self-absorption is neglected, the self-absorbed lines give rise to a measured absorbance weaker than expected leading to incorrect calibration procedures and consequently to poor estimation of trace metal concentrations. It is important to quantify the influence of self-absorption on the measured absorbance of the lines considered. The problem of self-absorption was developed for flame spectroscopy in early work by

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Omenetto et al [15]. Also, the self-absorption effects in the case of inductively coupled plasma (ICP) has been experimentally investigated [16]. The serious problem of self-absorption of optically thick lines can be treated parametrically on the basis of escape factor. A method is suggested, in this work to estimate quantitatively the effect of self-absorption for some resonance lines of nickel and some elements of environmental importance, by means of the optical escape factor. The method presented here has its associated concepts which were developed by Drawin and Emard [17], and Irons [18]. This method was also applied to calculate the escape factor in atomic absorption measurements [19]. In a recent work by Habib [20] the escape factor for bound-bound and free-bound nitrogen resonance lines in the case of SF<sub>6</sub>-N<sub>2</sub> plasma mixture have been calculated to quantify parametrically the influence of self-absorption.

The present paper is focused on the investigation of the absorption from a flame of nickel spectral lines at 232.0 and 352.3441 nm. For each line, the absorbance is measured using analyte solution with varying concentrations (10-100 mgL<sup>-1</sup>). At higher concentrations an atomic line can be significantly self-absorbed. A simple method is suggested in order to estimate quantitatively the self-absorption effects by means of escape factor. The escape factor has been used in this work to calculate the real absorbance. The calculated absorbance were used to best fit the experimental measure of the absorbance to reduce the nonlinearity observed in calibration curves. Also, best theoretical relations that fit the experimental data relating the measured absorbance and the concentration have developed. The main aim is then to obtain unfailing calibration procedure leading to the determination of absolute trace metal concentrations. An enhancement of the limit of detection was obtained at the upper as well as lower trace ranges. In order to verify the reliability of the approach, some environmental elements sodium, potassium, cadmium and zinc were also investigated on the basis of the escape factor method at the wavelengths 589.0, 422.673, 228.8, and 213.856 nm respectively.

## 2. THEORETICAL BACKGROUND

The measured absorbance is defined as :  $A = \log[I_\lambda(0)/I_\lambda(\ell)]$ , where  $I_\lambda(0)$  is the intensity at wavelength  $\lambda$  of the incident light and  $I_\lambda(\ell)$  is the intensity after having passed through the length  $\ell$  of the absorbing medium. On the other hand, the absorbance  $A$  is related to the atomic absorption spectrometer read out % absorption [21]. Then the absorbance could be written in terms of the probability of photon capture  $\Psi$  as:

$$A = \log\left(\frac{1}{1-\Psi}\right) \quad (1)$$

The escape factor  $\Lambda$  which is the mean probability of photon escape whose values lies between 0 and 1 may be defined in terms of the mean probability of photon capture  $\Psi$  which is the complement of  $\Lambda$  by the simple relation [18]  $\Lambda+\Psi=1$ . Consequently, a relationship exists between the absorbance and the escape factor

$$A = -\log(\Lambda) \quad (2)$$

This relation is similar to the relationship between absorbance and transmittance [22]. The escape factor is used here to calculate the absorbance according to Eq. (2). The calculated and the measured absorbance were equal as long as Beer's law is valid. In general, escape factors have been used to model the radiation transfer of spectral lines. An escape factor is a parameter which multiplies the transition probability to allow for the effect of photo-excitation on population densities. It is frequently convenient to treat the effect of self-absorption parametrically, as a reduction in the emission expected from an optically thin plasma to allow for the effect of opacity on the emitted lines. In FAAS experimental measure of the absorbance at lower concentrations and to reduce the nonlinearity observed in calibration curves at higher concentrations.

The dimensionless escape factor depends upon the normalized line profile  $P(\lambda)$ . It is thus depends on all the mechanisms of line broadening and given by [17]:

$$\Lambda = \int_0^\infty P(\lambda) \exp\left[-\tau_0 \frac{P(\lambda)}{P(\lambda_0)}\right] d\lambda \quad (3)$$

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where  $P(\lambda_0)$  is the value of the normalized line profile at the line center wavelength  $\lambda_0$  and  $\tau_0$  (dimensionless) is the maximum optical thickness i.e. the optical thickness at the line center (i.e. at  $\lambda = \lambda_0$ ), it is given by the Ladenburg relation [17]  $\tau_0 = \sigma N \ell$ , where  $\sigma$  ( $\text{m}^2$ ) is the Ladenburg cross-section given in SI units by  $\sigma = (e^2/4 \epsilon_0 m c) f_{lu}$ , where  $e$  and  $m$  are respectively the electron charge (C) and mass (kg),  $\epsilon_0$  is the permittivity of free space ( $\text{C}^2/\text{Nm}^2$ ),  $c$  is the speed of light (m/s),  $N$  is the number density ( $\text{m}^{-3}$ ),  $f_{lu}$  (dimensionless) is the oscillator strength of the transition and  $\ell$  (m) is the length of the emitting plasma region. The severity of self-absorption varies with the optical thickness. The greater the optical thickness the greater is the self-absorption. The optical thickness depends on the density of the absorbing species present which is related to the concentration of the element in addition to the spectroscopic parameters of the spectral line itself. From Eq. (3) it can be seen that the escape factor depends upon the line profile and thus of all the mechanisms responsible of line broadening. In flame at atmospheric pressure, the profile of the resonance absorption lines is determined by Doppler broadening due to thermal motion of the atoms and collision broadening due to collisions of atoms with each other and also with foreign atoms originating from a supply gas, resulting in Lorentz broadening. Since these line broadening effects act independently from each other, the spectral line shape is described by their convolution. Hence, the profile of the resulting absorption line has Voigt profile. In this case the escape factor for Voigt profile takes the form [17]

$$\Lambda = \Lambda^D + F(a, \tau_0) \Lambda^L \quad (4)$$

where  $F(a, \tau_0)$  is an error function of the Voigt  $a$ -parameter and the maximum optical thickness. Hence, the limit of the Voigt parameter  $a \rightarrow 0$  corresponds to a pure Doppler profile, and  $\Lambda \rightarrow \Lambda^D$ , while the limit  $a \rightarrow \infty$  corresponds to a pure Lorentz profile and  $\Lambda \rightarrow \Lambda^L$  holds. From the definition of the Voigt function it follows that in the limiting cases,  $a \rightarrow 0$  and  $a \rightarrow \infty$  the Doppler and Lorentz profiles are respectively recovered as well.

### 3. EXPERIMENTAL STUDIES

#### 3.1. Atomic absorption measurements

Because of popularity of the atomic absorption spectrometry for the determination of trace metals in lower and upper trace range of different samples, the details can be found elsewhere [23,24] among many others. The most essential points required to obtain low limit of detection will be presented here. Absorption was measured using a single beam Perkin-Elmer atomic absorption spectrometer model 2380. It is fitted with 10 cm long rectangular burner which gives a wedge shaped flame with 10 cm length and at a temperature of 2400 K. The acetylene flow rates was fixed at a constant pressure to read the maximum values of absorbance for different concentrations.

A nickel filled Perkin-Elmer hollow cathode lamp (HCL) with 10 mA operating current at the resonance lines 232.0 and 352.34 nm was used as a primary light source. Different concentrations of nickel aqueous salt solution ranging between 10-100 mgL<sup>-1</sup> with 3% H<sub>2</sub>SO<sub>4</sub> as a chemical modifier were prepared and sprayed into the air acetylene flame. The metallic vapor of free analyte nickel atoms are generated and probed by the radiation from the HCL at their characteristic wavelength, so the peak absorbance can be determined for each concentration.

The atomic absorption measurements are considered on the assumption that the resonance lines emitted from the HCL are Doppler broadened lines. In the flame two broadening mechanisms can occur independently: Doppler broadening due to thermal motion of free atoms and collision broadening due to random motion of the atoms which collide with each other and also with matrix components of samples. Since these line broadening effects act independently from each other, the resultant line shape can be considered by their convolution i.e. by Voigt profile.

### 3. 2 Determination of meta-stable state and resonant energy level population

The knowledge of the density of nickel is important for the estimation of the strength of the self – absorption effects. The numerical estimation of the number density of free atoms in the ground state responsible for absorption can be determined from experimental conditions. In analytical FAAS the density  $N$  of atoms in a given meta-stable or resonant state energy level is related to the absorption coefficient of the line probed at a wavelength  $\lambda$ , once this coefficient is integrated over the line profile since:  $\int k(\lambda) d\lambda =$

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$(\pi e^2/mc) Nf_{lu}$ . This integration tells us that the total absorption is constant for constant concentration, whatever the physical process that are responsible for the formation of the absorption line. For Voigt profile, N was related to the maximum absorption coefficient  $k_m$  ( $m^{-1}$ ) by the relation [25,26]:

$$N = k_m \sqrt{\frac{\pi}{\ln 2}} \frac{4\pi\epsilon_0 mc^2}{e^2} \frac{\Delta\lambda_L \Delta\lambda_D}{4\lambda_0^3 f_{lu}}$$

(5)

where  $\Delta\lambda_D$  and  $\Delta\lambda_L$  are respectively the Doppler and Lorentz full widths at half maximum (FWHM). In the case of nickel atoms the ground electronic state configuration has two additional sublevels, in addition to a meta-stable state with three sublevels. Therefore the total nickel density is the sum of the populations of these six low lying and meta-stable states. It is often necessary to relate the population of any given state to the total number density of atoms of that particular species. Consequently, the population  $n_j$  of an upper excited level  $j$  is related to the total number density  $N$  by the Boltzmann relation [27]:

$$n_j = \frac{Ng_j}{Z(T)} \exp[-(E_j/kT)] \quad (6)$$

where  $E_j$  the energy of the excited level  $j$ ,  $g_j$  the corresponding statistical weight,  $k$  Boltzmann constant,  $T$  is the absolute temperature and  $Z(T)$  is the electronic partition function of the corresponding species. The partition function was calculated by the relation of Galan et al [28].

## 4. RESULTS AND DISCUSSION

### 4. 1 Experimental results from the aspiration of FAAS measurements

Experimental results relating the measured absorbance  $A$  to the concentration  $C$  for the two Ni-resonance lines at 232.0 and 352.3441 nm are presented in Fig.1. The absorbance values for the 232.0 nm resonance line are significantly higher than the corresponding values for the line at 352.3441.0 nm over the entire range of concentration. The line at 232.0 nm has sensitivity approximately 1.8 times greater than that of the 352.3441 nm line. This may be due to the fact that this line has a transition probability



equal to  $6.9 \times 10^8 \text{ s}^{-1}$  corresponding to oscillator strength of 0.68. Thus, it provides the largest absorption.

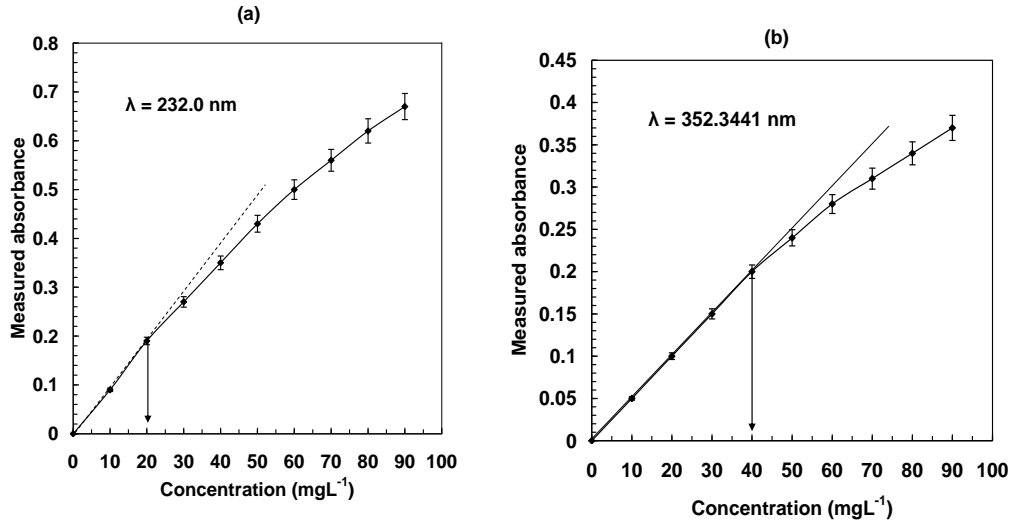


Fig. 1 The experimental calibration curves of nickel resonance lines at 232.0 nm (a) and 352.3441 nm (b). The error bars denote standard deviations (SD).

The most important result according to Fig. 1 is that the linear relationship between  $A$  and  $C$  does not hold for large  $C$  as expected from Beer-Lambert law. The inflection observed in Fig.1 occurs at the transition between an optically thin and optically thick (self-absorption) region. The inflection point for the two nickel lines occurs at 20 and 40  $\text{mgL}^{-1}$  respectively. This indicates the fact that both lines are to some extent, suffering from self-absorption which cannot be overlooked and must be treated carefully.

The relevant values of the Voigt  $a$ -parameter for nickel lines were obtained from the experimental curves of growth. For the line at 232.0 nm,  $a = 0.25$  and for the line at 352.3441nm,  $a = 0.15$ . These values indicate that the contribution from the Lorentz profile is small in both cases [17,29]. The main reason could be explained by the fact that as the Voigt  $a$ -parameter

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decreases the contribution of the far line wings to the total area becomes correspondingly less important and the absorption in far line wings is negligible.

#### **4. 2. Analytical characteristics of the FAAS measurements**

The precision of the present measurements, calculated as the limit of detection LOD, which is of extreme importance in AAS measurements. It is defined as the concentration of analyte required to give a signal equal to that of the blank plus three times the standard deviation of the blank. It is not always practical to perform multiple blank determinations, since the repetitive measurements are time and chemical consuming. In addition, it is a fact that there is no such material with zero concentration. Alternatively, the LOD could be calculated directly from linear regression analysis of the calibration data. The regression equations for nickel 232.0 and 352.3441 nm lines were obtained by direct aspiration in FAAS. The linear equations were,  $A=0.0072C+0.0472$ , the correlation coefficient  $R^2$  was 0.9913, and  $A=0.0043C+0.0102$  ( $R^2 = 0.9961$ ) for nickel 232.0 and 352.3441 nm respectively, where A is the absorbance and C is the metal concentration in  $\text{mgL}^{-1}$ . The LOD is then calculated from regression equation as  $\text{LOD} = 3S_{y/x} / b$ , where  $S_{y/x}$  is the standard deviation of the measurements and b the slope of the regression line. The limit of quantification (LOQ) which is the lowest concentration at which there is some confidence in the accuracy of the reported measurement was calculated as:  $\text{LOQ} = 10S_{y/x} / b$ . The LOD values were found to be 8.33 and 6.98  $\text{mgL}^{-1}$ , while the LOQ values were 25.3 and 23.25  $\text{mgL}^{-1}$  for nickel lines at 232.0 and 352.34 nm respectively. These values which indicate that 232.0 line is most sensitive in the UV spectral range, were worth than those obtained after self-absorption correction (Table 1).

#### **4. 3. Self – absorption quantification by the escape factor method**

For a wedge shaped flame with 10 cm length and at a temperature of 2400 K, it is found that the escape factor of the nickel spectral lines at 232.0 and 352.3441 nm is varying with metal concentration for Voigt profile as shown in Fig. 2. From this figure, it is clear that for  $C \leq 8 \text{ mgL}^{-1}$  the escape factor for 232.0 nm line is equal to 1.0 ( $\Psi = 0$ , i.e. 0.0 % absorption). As the concentration increases to 10  $\text{mgL}^{-1}$  the absorption becomes 5 % ( $\Lambda \approx 0.95$ ),

and then, the percent absorption increases up to 80.4 % at a concentration of 100 mgL<sup>-1</sup>. From these results one can deduce that the self-absorption phenomena cannot be neglected for this resonance line especially at higher concentrations. For the less sensitive line at 352.34 nm the escape factor is equal to 1.0 (i.e. 0.0 % absorption) even at high concentrations. This means that, the self-absorption phenomena for this line could be neglected for higher concentrations, up to 100 mgL<sup>-1</sup> or even more. This demonstrates the advantage of using less sensitive lines for nickel determination at higher concentrations in order to avoid problems associated with non-linear calibration curves.

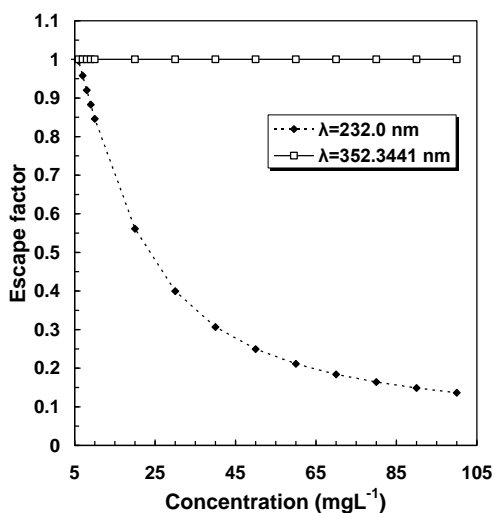


Fig. 2 The resonance escape factor for nickel resonance lines at 232.0 and 352.3441 nm as a function of analyte concentration assuming Voigt profile.

The escape factor has been used here to calculate the real absorbance using the relation  $A = -\log(\Lambda)$ . It should be clear that for conventional FAAS, the relation  $A = \log[I_{\lambda}(0)/I_{\lambda}(\ell)] = -\log(\Lambda)$ , holds as long as Beer-Lambert law is valid. The real absorbance was calculated using the corresponding escape factor given in Fig. 2. By a simple least square fitting the results obtained were compared with those for measured absorbance as depicted in Fig. 3.

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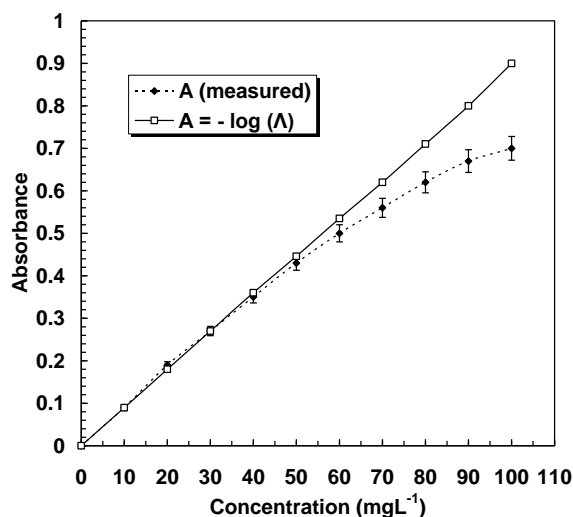


Fig. 3 The calibration curve for nickel resonance line at 232.0 nm.

The self-absorption is more significant for the measured absorbance as shown by a decreasing slope at high concentrations. Also, one may conclude from Fig. 3 that a simple least square fitting of the calculated real absorbance best fit the measured absorbance at low concentrations and is most suitable to reduce the nonlinearity in calibration curves at higher concentrations.

The escape factor has been used to reduce the nonlinearity observed in calibration curves at higher concentration in one hand and to best fit the measured absorbance at lower concentration on the other hand. The use of linear calibration of the real absorbance makes the procedures suitable for the reduction of non-linearity observed in calibration curves due to self-absorption. Consequently, the main problem of defining unfailing calibration procedures leading to the determination of absolute impurity concentrations was overcome.

The calibration graphs for nickel 232.0 and 352.3441 nm lines obtained after self-absorption correction were linear in the range of 8-100 mgL<sup>-1</sup> and 10-300 mgL<sup>-1</sup> respectively. The regression equations for nickel 232.0 and 352.3441 nm lines were  $A=0.0085C-0.0447$  and  $A=0.0002C+4E-6$  respectively. The correlation coefficient ( $R^2$ ) of every linear fit to the

calibration points was 1.0 or at least around 0.999. The characteristic concentrations calculated from the calibration shows lower sensitivity for the wider linear range. The typical analytical parameters of the calibration curves for the determination of nickel by direct aspiration in the present FAAS measurements were compared with those obtained after self-absorption correction in table 1.

Table 1 Comparison of the analytical parameters obtained by direct aspiration in FAAS before and after self-absorption correction.

Parameter	Before self-absorption correction		After self-absorption correction	
	232.0 nm	352.3441 nm	232.0 nm	352.3441 nm
Linear range (mgL <sup>-1</sup> )	10-100	10-100	10-100	10-500
Regression equation	A=0.0072C+0.0472	A=0.0043C+0.0073	A=0.0076C-0.051	A=0.0002C+4.0E-6
C. coefficient (R <sup>2</sup> )	0.9913	0.994	1.0	1.0
LOD (mgL <sup>-1</sup> )	8.33	6.98	0.21	0.017
LOQ (mgL <sup>-1</sup> )	25.3	23.25	0.697	0.056
RSD (%)	5.2	4.43	0.14	0.005

From the data given in table 1 we may conclude that for concentration  $C \leq 8.33 \text{ mgL}^{-1}$  the measured absorbance for nickel 232.0 nm line is treated as consistently emerges from the noise, but in this interval, there is low confidence of detection. For  $8.33 \leq C \leq 25.3 \text{ mgL}^{-1}$ , the measured absorbance should only be reported with error interval. The relative standard deviation (RSD) calculated as  $(100 \times S_{y/x} / A_{\text{aver}})$  was 5.2 %. Finally, for  $C \geq 25.3 \text{ mgL}^{-1}$ , the measured absorbance is reported as a measurement with high confidence of detection. Identical analysis for the weak line at 352.3441 nm were obtained, but the measured absorbance with high confidence of detection is at concentration above  $23.25 \text{ mgL}^{-1}$ .

The LOD and LOQ values observed for the nickel lines were worse than those found after self-absorption correction, and those obtained by pre-concentration methods [8-12]. The main reason is likely due to the fact that the linear calibration range was observed for nickel resonance lines studied up to  $100 \text{ mgL}^{-1}$ , while the maximum linear calibration range obtained by pre-concentration methods was only up to  $0.8 \text{ mgL}^{-1}$ . For that reason we have subdivided the whole range into many different ranges and calculated the LOD and LOQ in each interval. Fig. 4 shows the dependence of the

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LOD and LOQ for nickel line at 232.0 nm as a function of the range wideness. It is important to point out that the LOD potentially depends upon the wideness of range used. The LOD increases with wider ranges and decreases with narrower ones. It should also be clear that, for narrower ranges (0.01-0.4 mgL<sup>-1</sup>), not seen in Fig. 4, the value obtained for LOD was in good agreement with the value reported by Şahin et al [12] using pre-concentration method. Also, an enhancement of the LOD was obtained at higher concentrations by quantification of self-absorption on the basis of escape factor.

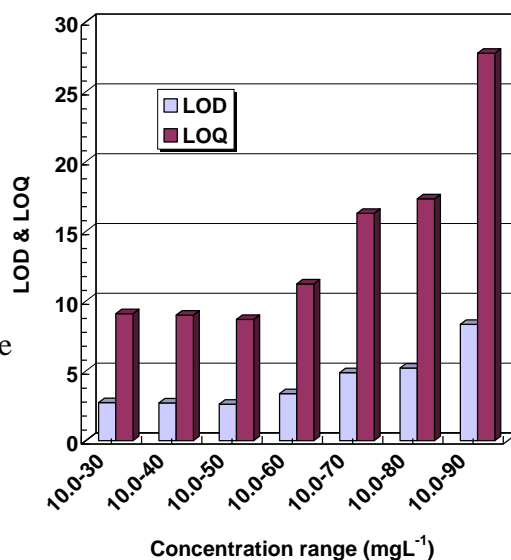
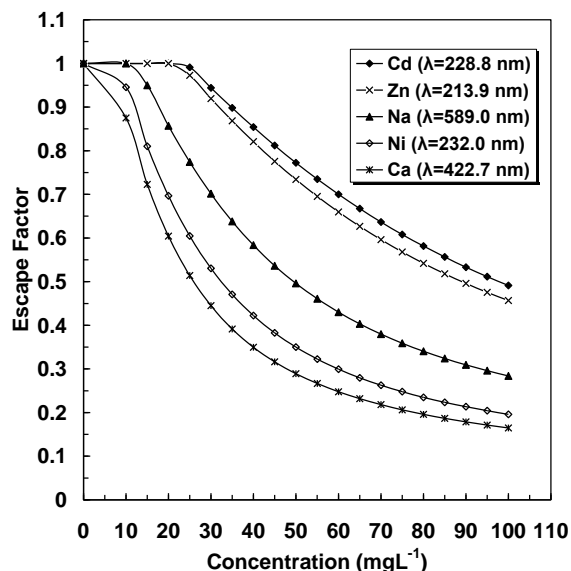


Fig. 4 The limit of detection (LOD) and the limit of quantification for the nickel.

The reliability of the approach was verified by applying the escape factor method to the environmental elements sodium, calcium, cadmium and zinc. The resonance lines at 589.0 for Na, 422.673 nm for Ca, 213.856 nm for Zn and 228.8 nm for Cd were chosen for the present investigations. The escape factor for the resonance lines of Na, Ca, Zn and Cd have been calculated assuming Voigt line profile (Fig. 5).

Fig. 5 The resonance escape factors for Cd, Zn, Na, Ni and Ca as a function of analyte concentration assuming Voigt profile.



This figure represents the variation of the escape factor as a function of the corresponding element concentration. In general, the increase of the element concentration induces an important decreasing of the escape factor and consequently an increase of the self-absorption of these resonance lines. Consequently, the self-absorption cannot be overcome at higher concentrations. The real absorbance [ $A = -\log(\Lambda)$ ] for each element under consideration has been calculated from the corresponding escape factor given in Fig. 5. Fig. 6 shows typical graphs of the real absorbance against the element concentration in the analyte solution. Accordingly, linear calibration was obtained for Na, Ca, Ni, Cd and Zn up to 85, 35, 100, 75 and 60 mgL<sup>-1</sup> respectively. The individual calibration curves were constructed with several points as absorbance versus element concentration. The correlation coefficient ( $R^2$ ) of every linear fit to the calibration points was 1.0 in each case or at least greater than 0.999. The linear regression equations for the calibration graphs were  $A = 0.012C - 0.021$  for Na,  $A = 0.0286C - 0.0064$  for Ca,  $A = 0.0076C - 0.0513$  for Ni,  $A = 0.0135C - 0.02$  for Cd and  $A = 0.0169C - 0.0302$  for Zn. The limits of detection as calculated

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according to calibration lines characteristics, the limits of quantification, the characteristic concentrations and the percent relative standard deviations (RSD %) were summarized in table 2, and compared with those found [30]. The accuracy of the proposed calculations was evaluated by comparing the results of LOD in the tested linear calibration ranges for Na, Cd and Zn with the results obtained using electrolyte cathode atmospheric glow discharge (ELCAD) by Gyö rgy et al [30]. The comparison of the LOD for the elements Na, Cd and Zn showed that the LOD and the wideness linear range were improved by calculating the real absorbance from the corresponding escape factor. The FAAS devices must exhibit low limits of detection allowing the measurement of low as well as high pollutant percentages. An enhancement of the LOD of the elements under investigation was obtained even at higher concentrations by quantification of self-absorption on the basis of escape factor. The characteristic concentrations of the analytes which means the amount of the concentration yielding an absorbance of 0.0044, ranges from 0.38 to 2.12. The characteristic concentrations reported in table 2 show higher sensitivity than those reported for ELCAD [30], except for Zn.

Fig. 6 Theoretical calibration curves for Na, Ca, Ni, Cd and Zn.

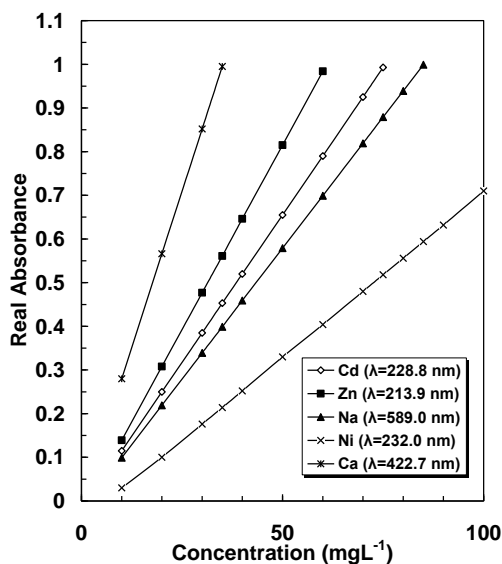




Table 2 Comparison of the analytical parameters obtained in the present work and the electrolyte cathode atmospheric glow discharge as an atom reservoir in atomic absorption spectrometry (ELCAD-AAS) [36].

Parameter	Na	Ca	Cd	Zn
Reference				
$\lambda$ (nm)	589.0	4226.7	228.8	213.9
Linear range (mgL <sup>-1</sup> )	1-85	0.1-35	2-75	1-60
This work				
	25-100	----	10-75	5-25
[36]				
LOD (mgL <sup>-1</sup> )	0.13	0.11	0.1	0.04
This work				
	9.2	----	3.4	0.9
[36]				
LOQ (mgL <sup>-1</sup> )	0.44	0.36	0.31	0.13
This work				
RSD (%)	0.1	31	0.11	0.04
This work				
Characteristic Concentration (mgL <sup>-1</sup> )	2.12	0.38	1.84	2.05
This work				
	5.3	---	2.0	1.4
[36]				

## 5. CONCLUSION

The reliability of conventional FAAS for quantitative trace metal analysis has been investigated in the upper trace range. It was successfully applied for the determination of nickel without pre-concentration or any chemical treatment. The reliable values of the LOD for each line were in satisfactory agreement with the wider linear range. The resonance escape factor for the two resonance lines of nickel at 232.0 and 352.34 nm has been calculated in order to quantify the effect of self-absorption on the measured absorbance for each line. The same method was successfully applied for the

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elements Na, Ca, Cd and Zn. The quantification of the self-absorption leads to the following important remarks.

(i) The self-absorption for nickel 352.3441 nm line is not very significant. This phenomenon was also reported for Na 330.3 nm line. consequently the less sensitive lines for all elements are most suitable for the element determination at higher concentrations.

(ii) The strong resonance lines are very suitable for element determination by conventional FAAS for the lower trace range.

(iii) The Escape factor method could be used to correct the effect of self-absorption on the measured line absorbance by a simple least square fitting.

(iv) The escape factor method could serve as a calibration guide for the measured absorbance and at the same time an avenue to quantify the self-absorption effects.

(v) The LOD is potentially dependent upon the linear range. For narrower linear ranges the LOD is small, while it is relatively large for the wider one. Finally, the escape factor mainly depends on the number of atoms responsible for absorption. Apart from theoretical investigations which should progress in this direction, extensive experimental studies should still be made. They should concern mechanisms, namely atomic vaporization and sample introduction into the system. The nebulization process is usually insufficient. Consequently, most of the sample is not transported to the atomizer and there is a great dilution of the sample by flame gases. The resulting analyte concentration in the measurement zone is relatively low.

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