



Determination Method of High Content of Nickel in Ferronickel and Various Alloys Using Atomic Absorption Spectrometry

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Abstract: The atomic absorption spectrometric method was applied to the determination of the high concentration of Nickel in ferronickel and other ferroalloys containing nickel. The influences of experimental parameters, such as wavelength, slit width, burner height and fuel flow rate were evaluated. Instrumental conditions such as burner height, wavelength, fuel flow rate and slit width have been optimized in a manner to achieve minimum absorption signal with low background. The effects of several physical conditions like slit width, fuel gas flow rate; burner height and calibration on the change in the absorbance of nickel under the optimized conditions were also studied. The accuracy of the procedure was sufficient and evaluated in comparison with other established methods such as WDXRF and classical procedure by gravimetric method - Dimethylglyoxime (DMG). The applied procedure could be successfully applied for the determination of nickel in ferronickel and other ferroalloys. Based on that what we explained above we can confirm the main aim of this kind of study is: The Atomic Absorption Spectrometry is well known for good accuracy determination in low concentration (ppm or ppb), but we can use also this technique and method for determination in high concentration (content) like in this paper.

Keywords: *High concentration, nickel, ferronickel, alloys, FAAS, WDXRF, DMG.*

Introduction

The chemical element of nickel is an important alloying metal, which is mainly used for steel refining. The great importance of nickel lies in its ability when alloyed with other elements like Cr, Cu, Mo, Be, Fe, Mn, *etc.*, to increase a metal's strength, toughness and corrosion resistance over a wide temperature range. Nickel is essential to the iron and steel industry and nickel containing alloys has played a key role in the development of the materials for the aerospace industry. In these alloys, the concentration of nickel is in percentages and its accurate measurement is necessary for quality assistance. For the determination of nickel in ferronickel and other alloys, different analytical methods are used. Some of them are classical (gravimetric) method by Dimethylglyoxime (DMG), flame Atomic Absorption Spectrometry (FAAS), X-ray Fluorescence Spectrometry (XRF), Optical Emission Spectrometry (OES), inductively coupled plasma combined with atomic emission spectrometry (ICP-OES) and neutron activation analysis (NAA). However, flame atomic absorption spectrometry (FAAS) is one of the most extensively used methods for determining various elements including nickel with significant precision and accuracy. The Atomic Absorption Spectrometry is well known for good accuracy determination in low concentration (ppm or ppb), but we can use also this technique and method for determination in high concentration (content) like in this paper.

Moreover, this analytical technique is remarkable for its selectivity, rapidity, simplicity and fairly low operating cost. Nonetheless, in some cases, there are many difficulties in exactly determining of nickel in ferronickel due to excessive dilution of the sample solutions which results in poor accuracy and precision. To avoid the excessive dilution of sample solutions different effort have been made such as reducing the path length by rotating the burner head and then using an alternative wavelength having a lower absorptive. Also the aim of the present work was to investigate the application of less sensitive absorption line for the determination of the high concentration of nickel in ferronickel alloys and other ferroalloys like nickel base alloys and low alloy steel, using the optimized parameters of FAAS. Results which are given during this study are compared with other method and technique of determination like XRF and DMG. Those results are into analytical margins of the results in

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accordance with each other.

Materials and Methods

Apparatus

We have worked with equipment by producer Perkin Elmer - USA, model: AAnalyst 400 Atomic Absorption Spectrometer (AAS) with four hollow cathode lamp positions equipped with Deuterium background correction was applied for the determination of the nickel in ferronickel and other alloys using a nonlinear through zero calibration method. 10 cm single-slot burner head was used for air-acetylene operation. Lumina hollow cathode lamp of nickel from Perkin Elmer was used as radiation source. Also, the tested samples are analyzed in X-ray Fluorescence Spectrometry (XRF) by producer Thermo Scientific - Switzerland, model: ARL 9900.

Reagents and solutions

All reagents were of highest available purity (p.a.) from Merck producer. High purity single stock solutions of all elements 1000 g/ml \pm 0.03 g/ml were obtained also from Merck. Dilute standard solutions were prepared by dilution of the stock solutions. All tests and calibrations were performed in 1% v/v nitric acid solution. Double-distilled water for solution preparation was obtained using an Electrical Heating Stainless Re-distillation Appliance Model ZLSC produced in Poland. Glassware was cleaned in dilute nitric acid (1+1) followed by repeated rinses with water.

Procedure

0.1000 – 0.2000g samples were placed into 400 ml beakers and were digested according to the literature. Added 10ml dilute (1:1) nitric acid care fully down the sides of the beakers, using a measuring pipette. Boil the solutions in the hood until formation the red dish brown nitrogen dioxide gas ceases. Then added approximately 5ml concentrated perchloric acid. Sample evaporates in the sand bath until the appearance of salts but not drying up. Cool to room temperature and added 5 ml of concentrated hydrochloric acid, then added hot deionized water to 200 ml and heat gently until all salts dissolve. If any residue is present (probably silica, carbon) filter immediately through a medium porosity filter paper and wash the precipitate with water. The resultant solutions were transferred quantitatively to a 1000 ml volumetric flask and filled with 1% nitric acid up to the line. The solutions were aspirated into air-acetylene flame using the optimized instrumental parameters given in Table 1, in order of deionized water, standards, sample blank and samples. The signal evaluation is made by subtracting the signal of blank from the signals of the samples.

Table 1: Optimized instrument operating conditions used for the determination of the nickel

Parameter	Value
Spectrometer	Perkin Elmer A Analyst 400
Instrument mode	Absorbance, peak height
Measurement mode	Integration (3 seconds)
Resonance absorption line (nm)	341.48
Slit width/height (nm)	1.8/0.6
Lamp current(mA)	25
Burner height (mm)	20.0
Type of burner	Standard*
Oxidant gas (air) flow rate (L/min)	10.00
Fuel gas (C ₂ H ₂) flow rate (L/min)	2.50
Delay time (sec.)	3.0
Measurement time (sec.)	3.0
Calibrations Type	Nonlinear Through Zero

Results and Discussion

Optimizing the parameters of FAAS is essential in order to obtain satisfying results by the determination of the high content of nickel in ferroalloys. Therefore, various instrumental parameters such as resonance absorption line, slit width and fuel gas flow rate were optimized by aspirating 20 mg/L.

Effect of physical parameters on nickel absorption

Selection of absorption line

Hollow-cathode lamps are a type of discharge lamps that emit a number of resonance lines. As known, the main resonance line of analysis provides the best sensitivity or the best signal-to-noise ratio. Therefore, it is set to the device to measure low analyte sample. For a high concentration of nickel samples is to use a less sensitive analysis line. The degree of absorption varies according to the resonance, leading to variation in the sensitivity of the line. Furthermore, the sensitivities of some of the nickel solution into an air-acetylene flame. The selection of the instrumental parameters which produce minimum and reproducible absorption signal with low background was a criterion for its optimization.

The major resonance lines were checked by measuring the absorption of 20 mg/L of nickel solution. The absorption was recorded at resonance lines of 232.00 nm, 303.79 nm, 323.30nm and 341.48 nm by using the fixed conditions of slit width/height (1.8/0.6), oxidant gas flow rate (10 L/min) and fuel gas flow rate (2.5 L/min). The results are shown in Figure 1. From resonance lines which are studied, the line at 341.48 nm is selected as line with four-fold less sensitivity and is selected to use regarding the optimization of other parameters.

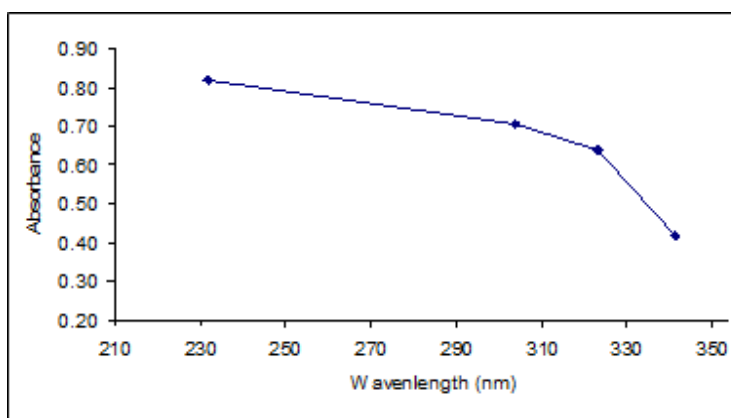


Figure 1. Effect of wavelength on the absorption of 20 mg L⁻¹ nickel in air-acetylene flame

Effect of slit width

The effect of different slit width at 20 mm burner height and 2.5 L/min. flow rate with a nickel solution of 20 mg/L at 341.48 nm indicates that there is a significant effect on nickel absorption at different slits. The table number 2 shows that the minimum absorption was observed at a spectral slit of 2.7 nm. Therefore, the slit width of 1.8 nm as in recommended conditions is taken for the current experiment.

Table 2. Effect of slit width on the absorption of 20 mg/L nickel solution at 341.48 nm

Concentration (ppm)	Absorbance	Slit width (nm)
20	0.43	1.8
20	0.40	2.7

Effect of fuel gas flow rate

The atomization process is affected in a complex way by variations in flame temperature which is dependent upon fuel to oxidant ratio. Higher temperatures tend to increase the total atom population of the flame and sensitivity.

Effect of variation of burner height

As known at room temperature and at a temperature obtained by most flame atomizers the number of atoms in the excited state is a very small fraction of those in the ground state. Also, flame temperature determines the relative number of excited and unexcited atoms in a flame. Furthermore, the sensitivity of absorption in the atomic absorption measurements will be proportional to the number of ground state atoms present in rate was optimized by recording the absorption signal of 20 mg/L of nickel solution using the fixed oxidant flow rate of 10 L/min and other optimized instrumental parameters. In figure 2 are presented the results of changing the fuel gas flow rate from 2.0 to 3.0

L/min, which's shows that the minimum absorption was observed at a fuel gas flow rate of 3.0 L/min, with a considerable fluctuation of the signal, so that the gas flow rate of 2.5 L/min as well as expected in recommended conditions, considered to be suitable for present study.

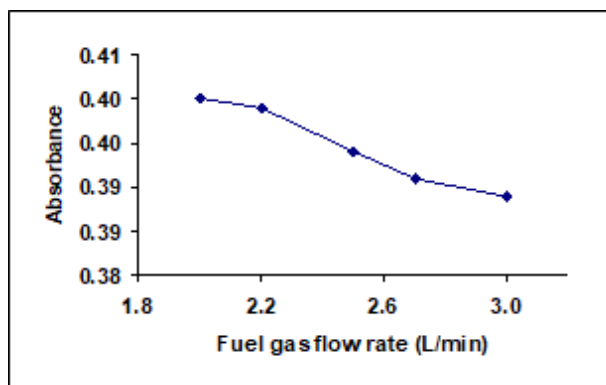


Figure 2. Effect of fuel gas rate on the absorption of 20 mg/L nickel solution at 341.48 nm

The flame irradiated by the beam of light emitted from hollow cathode lamp. The formed atoms are distributed in an unequal density within the flame profile; wherefore this parameter was also optimized for its minimum sensitivity. Under the optimized wavelength (341.28 nm) and slit width (1.8 nm) was recorded the signal of 20 mg/L of nickel solution by varying the burner height from 5.0 to 20.0 mm. The oxidant and fuel gas flow rate used were 10 and 2.5 L/m respectively.

The founded results are presented in figure 3, which shows that the minimum absorption was observed at the burner height by 24.0 mm, but the signal was unstable which leads to poor precision. Hence, the burner height of 20.0 mm i.e., the next least sensitive position of burner height was taken as appropriate and used in all the following measurements.

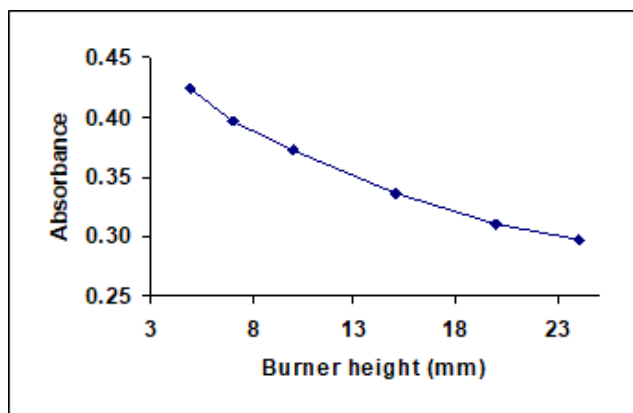


Figure 3. Effect of burner height on the absorption of 20 mg/L nickel solution at 341.48 nm

Calibration and Sensitivity

Sensitivity (for atomic absorption only) is defined as the concentration of an element (in mg/L) necessary to produce a signal of 1% absorption (0.0044 absorbance units), was determined under the optimized conditions and was found to be 19 mg/L of nickel. The detection limit is defined as the concentration of nickel that gives a signal three times the value of the standard deviation of ten determinations of blank, was determined to be 4.7 µg/L.

A calibration curve was constructed for the determination of nickel, in ferronickel and in other ferroalloys according to the recommended conditions under optimized parameters (Table 1 above). A correlation between absorption and nickel concentration (calibration curve) is shown in Figure 4. The calibration curve for nickel had a correlation coefficient R^2 value of 0.9972, showing a successfully linear plot of concentration vs. absorbance. The regression equation for nickel determination comes out to be: $y = 0.0096x + 0.0457$. The best results are obtained by working in the linear range from 10 to 20mg/L.

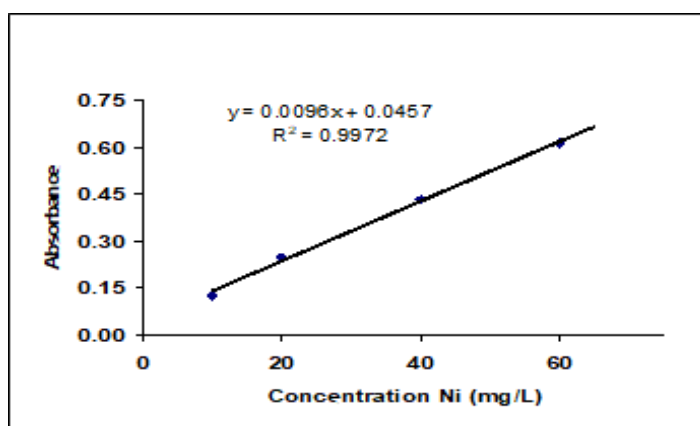


Figure 4. Calibration curve line for nickel

Method validation

The validity of this nickel determination procedure by AAS was checked by analyzing of several samples for their nickel contents with different analytical techniques such as X-ray fluorescence spectrometry (XRF) and classical gravimetric method by Dimethylglyoxime (DMG). The comparison of the results with different analytical techniques is presented in table 3 which is into analytical margins of the results in accordance with each other. The data presented in Table 3 shows that the established method can be used to the samples having low as well as high concentration of nickel in different matrices.

Table 3: Comparison of FAAS results for nickel with other analytical methods

Sample No.	CRM Sample	The concentration of nickel (%)		
		AAS	XRF	Gravimetric (DMG)
1	High-Nickel Steel 1158	35.97± 0.51	36.06± 0.21	35.94 ± 0.9
2	Ferronickel JSS 760-3	19.62 ± 0.09	19.60± 0.12	-
3	Ferronickel 1016/2	22.94 ± 0.27	22.96± 0.08	22.90 ± 0.5
4	Low alloy steel No. 405/1	0.212 ±0.03	-	-

*CRM – is Certified Reference Material

Analysis of various alloys

The current method was applied for the analyzing of nickel in fifteen samples of various types of alloys such as ferronickel alloys, low alloy steel and nickel base alloy. The results are presented in the Table 4. Those results are into analytical margins of the results in accordance with each other.

Table 4: CRM and IS standard samples for AAS checked with certified values

S. No.	Name of sample	CRM & IS Sample code	Certified	Ni (%)
				Found (Analyzed by AAS)
1	High-Nickel Steel	NIST CRM 1158	36.053 ± 0.03	35.97± 0.51
2	Ferronickel*	CRM JSS 760-3	19.56 ± 0.05	19.62 ± 0.09
3	Low alloy steel	BCS CRM 405/1	0.22 ± 0.01	0.212 ± 0.03
4	Iron base alloy	CRM CTIF FA 10	20.05 ± 0.06	19.99 ± 0.33
5	Ferronickel SKF 3F	SKF CRM 3F	10.37± 0.05	10.43 ± 0.13
6	Aust. Cast Iron ¹	BAS RM NIRM 6	26.70 ± 0.30	26.58 ± 0.32
7	Austenitic Cast Iron ²	CRM CTIF NR 3-2S	24.63 ± 0.14	24.34 ± 0.39
8	Ferronickel ¹ 1016/2	IS* 1016/2	22.96 ± 0.18	22.94 ± 0.27
9	Ferronickel ² A4168	IS* A4168	32.44 ± 0.23	32.51 ± 0.73
10	Ferronickel ³ A4203	IS* A4203	17.52 ± 0.18	17.53± 0.56
11	Ferronickel ⁴ A4189	IS* A4189	29.76 ± 0.20	29.69 ± 0.47
12	Ferronickel ⁵ A3949	IS* A3949	18.46± 0.17	18.45 ± 0.47
13	Ferronickel ⁶ 383/1	IS* 383/1	28.12± 0.15	28.10 ± 0.55
14	Corrosion resistant. cast iron	MBH RM 11S2CR2-D	18.00 ± 0.20	18.24 ± 0.57
15	In coloy type alloy (cast)	MBH RM 23X 8002-E	32.10 ± 0.14	32.14 ± 0.14

IS*- internal standard

Conclusions

The FAAS method described is suitable for the determination of nickel in ferroalloys as well as in ferronickel. Flame AAS is widely used for analysis of ferroalloys because of its simplicity, effectiveness and relatively low cost. Another advantage of this method is a relatively high degree of freedom from interference from its environment i.e. by the presence of other elements. However, by analyzing of the pure ferronickel a large excess of iron causes enhancement and calibration standards should be matched to the concentration of this element in the analyzed sample. This method is applicable to samples containing low as well high nickel contents in various matrices. Another advantage of this method is the small number of volumetric operations leading to higher precision and a low standard deviation. For monitoring of the production process, this technique should only be seen as a temporary alternative of established techniques like XRF or OES in which sample preparation takes only a few minutes. It is well known the AAS is very accurate and method of determination by this equipment is very accurate in small concentration range ppm or ppb.

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