

Analysis of Nickel Steel Alloys Using Inductively Coupled Plasma Atomic Emission Spectrometry Technique

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Quality Assurance Manager - Ministry of Higher Education and Scientific Research

ksziara@yahoo.co.uk

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Abstract

Steel and its alloys have many applications in industry and life in general. Their types and characteristics depends on the types and the amounts of elements present. Therefore, good quality measurements are essential for manufacturing industry to control steel products and processes quality. The objective of this study was to determine the elemental composition of Nickel steel alloys and their concentration. Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) was used for the analysis. Analytical results achieved at maximum wavelengths for Nickel 231.604nm, Chromium 267.716nm, Manganese 257.610nm, Silicon 251.611nm and Cupper 324.754nm show that concentrations obtained are in line with those for the reference standard used. Detection limits between 0.00004 to 0.0003 wt% and RSDs of 1.9 – 3.5 % were achieved for the elements analyzed in this study.

Key Words: Atomic Emission Spectrometry (AES), Inductively Coupled Plasma (ICP), Analysis of Nickel Steel Alloys.

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تحليل سبائك النيكل الفولاذية باستخدام تقنية مطيافية الانبعاث الذري / بلازما الحث المقترن ICP-AES

خالد شناوة زيارة

مدير قسم ضمان الجودة - وزارة التعليم العالي والبحث العلمي

الخلاصة

للفولاذ وسبائكه تطبيقات عديدة في الصناعة والحياة بصورة عامة. انواعه وخصائصه تعتمد على نوع وكميات العناصر الموجودة فيه. لذلك فإن القياسات ذات النوعية الجيدة ضرورية جدا للشركات المصنعة للفولاذ لمراقبة عمليات وجودة منتجاتها. يهدف هذا البحث الى تحديد مكونات سبائك النيكل الفولاذية ونسبها باستخدام تقنية مطيافية الانبعاث الذري / بلازما الحث المقترن - ICP AES. اظهرت النتائج التحليلية عند الطول الموجي الاعظم لعناصر النيكل Ni 231.604 nm والكروم Cr 267.716 nm والمنغنيز 257.610 nm والسيليكون Si 251.611 nm والنحاس Cu 324.754 nm ان النسب التي تم الحصول عليها لهذه العناصر تتفق مع تلك المستخدمة للمعيار المرجعي المستخدم. حدود الكشف لهذه العناصر كانت بين 0.00004 الى 0.0003 % اما الانحراف المعياري النسبي RSD فقد تراوح بين 1.9 – 3.5 %.

الكلمات المفتاحية: مطيافية الانبعاث الذري (AES)، بلازما الحث المقترن (ICP)، تحليل سبائك النيكل الفولاذية.

Introduction

Steels and its alloys are the most widely used metals in industry and have a wide range of uses in industry and life in general which varies from constructional to a very sophisticated medical tool. Nickel Steel alloys are the most important among all the steel alloys due to their use in various places all around the world. It is formed when some percentage of nickel is added to the steel. This type of steel alloys are used for making storage cylinders for liquefied gases, heavy forgings, turbine blades, highly stressed screws, bolts, nuts, making shafts, gears, propeller shafts, and keys. The presence of some type of elements and their concentration can enhance or change the properties of the steel to suit the requirements of the application they are used for. For instance, addition of Carbon can improve the hardness of cutting edge whilst the addition of Chromium, Nickel and Manganese give corrosion resistance. According to the World Steel Association, there

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are over 3500 different grades of steel, each type has unique physical, chemical, and environmental properties. These types of steels can be classified into four groups based on their chemical composition (Alloy, Carbon, tools and stainless steels). Alloy steels contain alloying elements such as Nickel, Chromium, Silicon, Copper, Titanium, Manganese and Aluminum. These alloying elements present in varying amounts in order to control the steel's properties such as hardness, strength, corrosion resistance, etc. Applications for alloys steel include power generators, pipelines, transformers, auto parts and electric motors [1].

The to many types of steels with diverse properties make both process and quality control are extremely important for the industry, as these properties depends on the types and the amounts of elements present. Therefore, the analysis of steel and its alloys has become a common application in many laboratories around the world. The analysis of content levels ranges from several tens of percent to ppm level requires a very reliable analytical technique capable of high sensitivity, a wide dynamic range, good detection limit and high accuracy. A variety of techniques have been used for elemental analysis of steels such as Arc/Spark optical Emission Spectroscopy (A/S OES) [2] and X – Ray fluorescence (XRF) Spectroscopy [3, 4]. These techniques offer fast analysis with no or little sample preparation required, and can be provided as portable units, for maximum flexibility. These techniques are considered non-destructive in that the metal steel alloys are left unchanged after analysis. However, there are limitations associated with the use of these techniques for steel analysis, both in the terms of sensitivity and the total number of elements analyzed [5].

Inductively coupled plasma atomic emission spectrometry ICP-AES can provide significant advantages to conventional solid-sampling techniques. Although the sample preparation step is more time-consuming and requires the use of concentrated acids, the analysis can provide much improved sensitivity, better detection limits, high accuracy and a wider linear dynamic range. This in turn has made ICP – AES one of the most common analytical techniques for the analysis of a variety of sample types such as metals, biological, archaeological, medical and environmental samples. In this technique a plasma source with temperature of 6000 to 10 000 K is used to

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dissociate the sample into its constituent atoms or ions, exciting them to a higher energy level. When return to their ground state, these atoms and ions emit photons of a characteristic wavelength depending on the element present. This light is then recorded by an optical spectrometer. When calibrated against standards the technique provides a quantitative analysis of the original sample [6 – 13].

Experimental Section

1. Standards and Sample Preparation

Nickel Steel Alloy 1000mg of was accurately weighed in a microbalance. Then 5ml of Hydrofluoric acid (47-51%, Trace Metal, Fisher Chemicals), 10ml HNO₃ (67-70%, Trace Metal, Fisher Scientific) and 10ml of HCl (34 – 37%, Trace Metal, Fisher Scientific) were carefully added. The mixture then heated on a sand bath until the sample is dissolved and then transferred to plastic 100ml conical flask. Extra care was taking to make sure that the temperature does not exceed 55°C to avoid the loss of Si during digestion of SiF₆, which is volatile. Dilution to volume was made using deionised water to obtain a 10000mg/L solution. Finally, to obtain a 2500mg/L solution suitable for analysis, A 25ml of the 10000mg/L solution was accurately transferred to a 100ml conical flask and dilution to volume was made using Deionized water. For the sample blank, 1250mg of high purity iron powder (99.99% made by Johnson Matthey) was accurately weighed in 250ml PTFE beaker. Then 6.5ml of HF, 12.5ml HNO₃ and 12.5ml of HCl were carefully added. The mixture then heated on a sand bath until the iron is dissolved and then transferred to PTFE 500ml conical flask. The mixture was then diluted to volume with Deionized water to obtain a solution of 2500mg/L and was used as a sample blank. Iron concentrations in Standards (1-5) were prepared the same way as the blank solution to obtain iron concentrations mentioned in Table (1). Standard solutions of analytical elements were added in stepwise fashion to prepare calibration curve samples. The standards prepared are shown in Table (1) below:

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Table 1: Standard Concentration

| Element | Blank | Standard 1 | Standard 2 | Standard 3 | Standard 4 | Standard 5 |
|-----------|----------------------|---------------------|---------------------|--------------------------|---------------------|---------------------|
| Nickel | | 2.5 mg/L 0.1% | 12.5 mg/L 0.5% | 25 mg/L 1% | 125 mg/L 5% | 250 mg/L 10% |
| Chromium | | 2.5 mg/L 0.1% | 12.5 mg/L 0.5% | 25 mg/L 1% | 125 mg/L 5% | 250 mg/L 10% |
| Manganese | | 1.25 mg/L 0.05% | 2.5 mg/L 0.1% | 12.5 mg/L 0.5% | 25 mg/L 1% | 50mg/L 2.0% |
| Silicon | | 0.25 mg/L 0.01% | 1.25 mg/L 0.05% | 2.5mg/L 0.1% | 12.5 mg/L 0.5% | 25 mg/L 1.0% |
| Copper | | 0.25 mg/L 0.01% | 1.25 mg/L 0.05% | 2.5 mg/L 0.1% | 12.5 mg/L 0.5% | 25 mg/L 1.0% |
| Iron | 2500 mg/L 100% | 2488 mg/L 99.52% | 2458 mg/L 98.32% | 2420.5 mg/L 96.82% | 2188 mg/L 87.52% | 1888 mg/L 75.52% |

2. Technique Used

ICP – AES with Meinhard nebulizer [14] and Scott – Fassel double pass spray chamber [15, 16] for sample introduction has been used in this study to ensure that only small droplets reach the plasma. The plasma was imaged at 1:1 ratio onto the entrance slit of the spectrometer with a fused silica lens (20 cm in focal length; 5 cm diameter). The output of the photomultiplier tube was fed to potentiometric chart recorder with a 20 k Ω load across the input to act as a current to voltage convertor. Table (2) describes the instrumentation used with the operating conditions listed at Table (3).

Table 2: The Instrumentation Used in This Study

| | |
|--------------------------------------|---|
| Radio Frequency (RF) Generator | Plasma – Therm Inc. , Kresson, NT, USA, Type 1500 D, 1.5 KW, 27.12 MHz. |
| Plasma Torch | Demountable Fused Silicon Torch Fitted into a Brass Base. |
| Optics and Spectrometer | Single Channel, 1 Plane Grating Spectrometer (Spex Industries Inc., Metuchen, NJ, USA). RLD 4 Å / mm. |
| Detection System | EMI 9789 QB photomultiplier tube (EMI, Hayes, Middlesex). |
| Readout | BBC Goerz Metrawatt Servogor 120 Potentiometric Chart Recorder. |
| Sample Introduction Technique | |
| Type of Nebulizer | Meinhard |
| Type of Spray Chamber | Scott – Fassel Double Pass. |

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Table 3: Operating Conditions and Parameters Used

| Parameter | Elements Analyzed | | | | |
|--------------------------------------|---------------------|-----------------------|------------------------|----------------------|---------------------|
| | Nickel 231.604nm | Chromium 267.716nm | Manganese 257.610nm | Silicon 251.611nm | Copper 324.754nm |
| Radio Frequency (RF) Generator Power | 1, 100 Watt | 1000 Watt | 1000 Watt | 900 Watt | 1000 Watt |
| Coolant Gas Flow Rate | 10 L/min Ar | 11 L/min Ar | 10 L/min Ar | 11 L/min Ar | 12 L/min Ar |
| Auxiliary Gas Flow Rate | 0.2 L/min Ar | 0.3 L/min Ar | 0.2 L/min Ar | 0.4 L/min Ar | 0.2 L/min Ar |
| Injector Gas Flow Rate | 1.1 L/min Ar | 1.0 L/min Ar | 1.0 L/min Ar | 1.1 L/min Ar | 1.0 L/min Ar |
| Observation Height | 11mm a.l.c | 10mm a.l.c | 12mm a.l.c | 10mm a.l.c | 12mm a.l.c |
| PMT Voltage | 1KV | 1KV | 1KV | 1KV | 1KV |
| Entrance and Exit Slit Width | 0.02 mm | 0.02 mm | 0.02 mm | 0.02 mm | 0.02 mm |
| Reciprocal Linear Dispersion | 0.4 nm/mm | 0.4 nm/mm | 0.4 nm/mm | 0.4 nm/mm | 0.4 nm/mm |

Results and Discussion

The constituent elements in Nickel steel alloy BCS 222 have been analyzed under the conditions listed in Table (3) using ICP – AES. Wavelength selection for each element analyzed, the line with the highest sensitivity was used, as listed in the Table (4). Calibration curves for Ni 231.604nm, Cr 267.716nm, Mn 257.610nm , Si 251.611nm and Cu 324.754nm are shown in Figures 1 -5 respectively.

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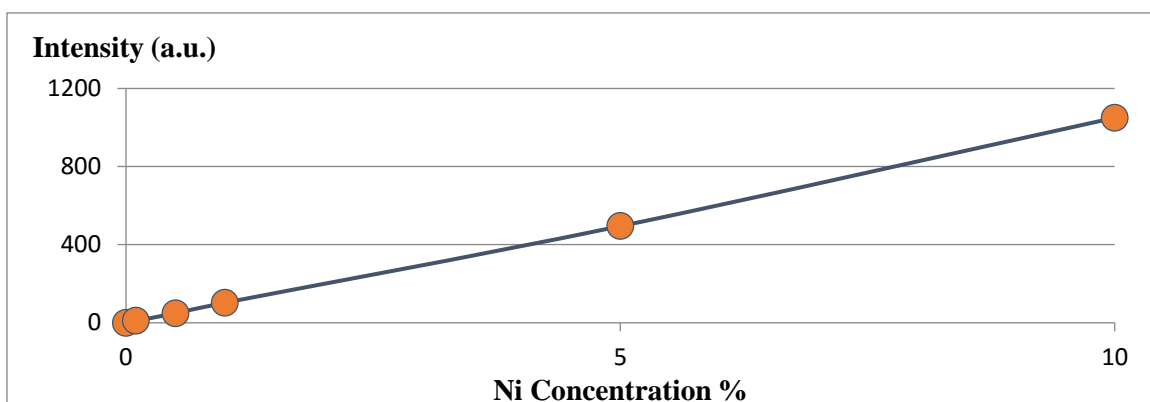


Figure 1: Calibration curve for Nickel in Nickel Steel Alloy BCS 222 at 231.604nm

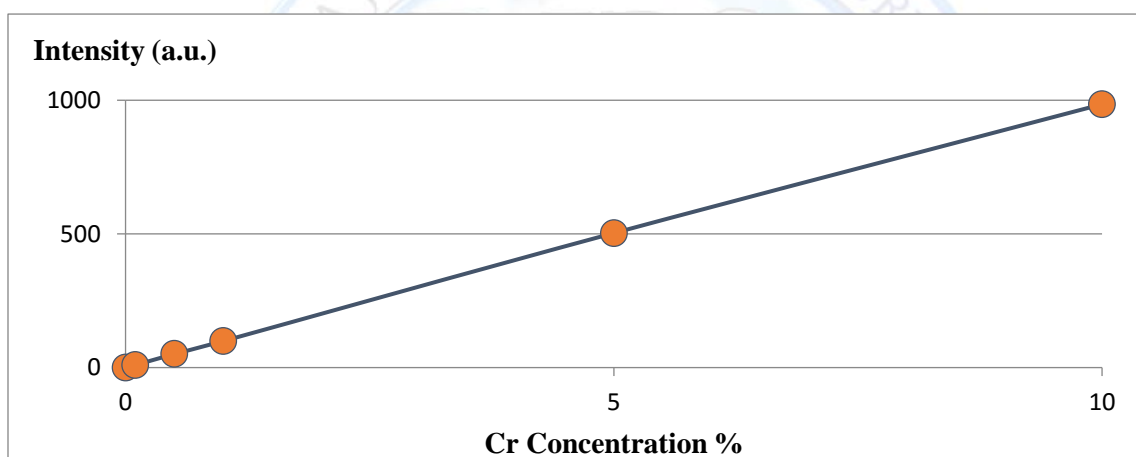


Figure 2: Calibration curve for Chromium in Nickel Steel Alloy BCS 222 at 267.716nm

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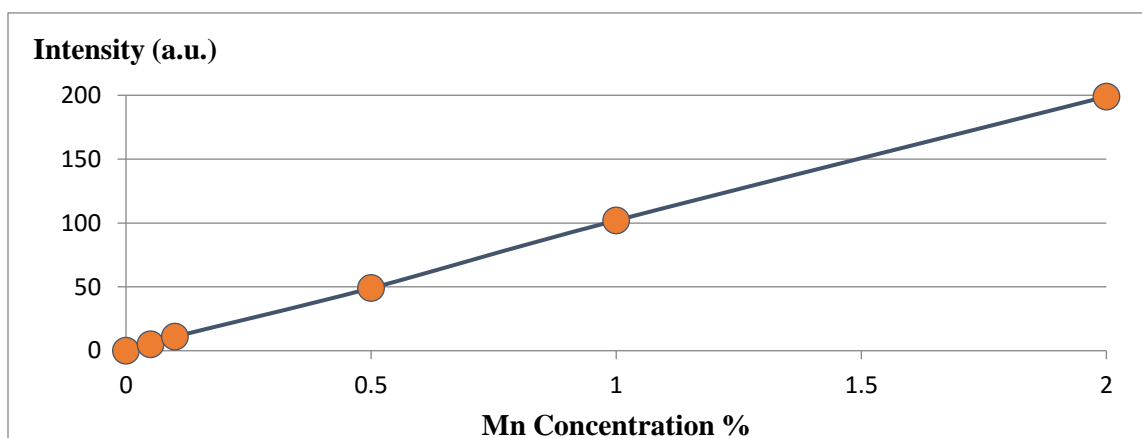


Figure 3: Calibration curve for Manganese in Nickel Steel Alloy BCS 222 at 257.610nm

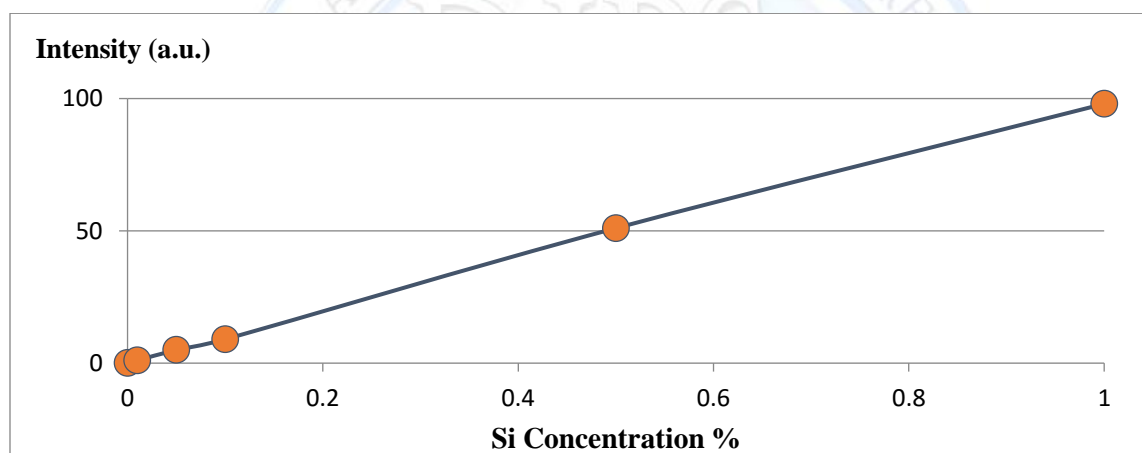


Figure 4: Calibration curve for Silicon in Nickel Steel Alloy BCS 222 at 251.611nm

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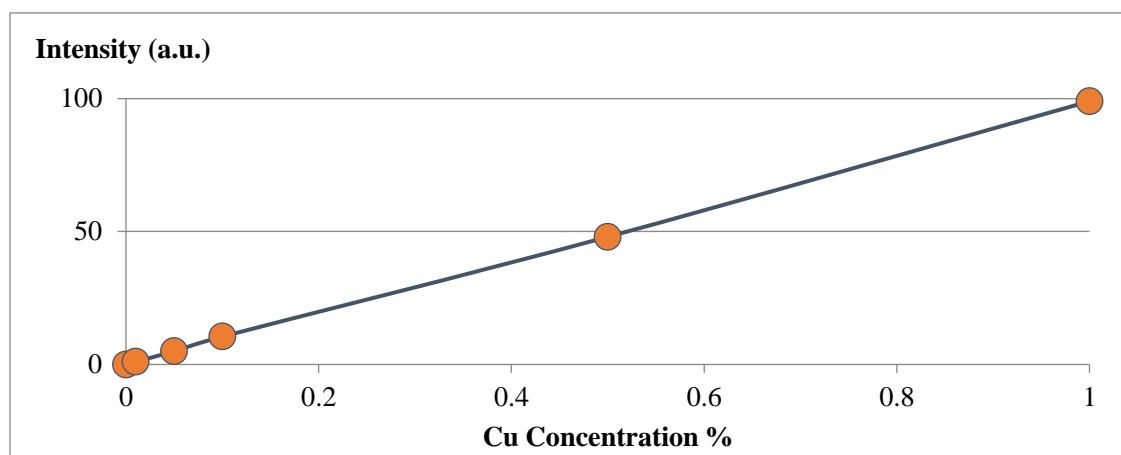


Figure 5: Calibration curve for Copper in Nickel Steel Alloy BCS 222 at 324.754nm

The summary of the analytical results achieved for the analysis of Nickel Steel BCS 222 are presented in table (4).

Table 4: Analytical results for the analysis of Nickel Steel BCS 222

| Element / Wavelength (nm) | Detection Limit (wt%) | Measured Concentration (%) | #Certified Values (%) | Reproducibility *RSD (%) |
|---------------------------|-----------------------|----------------------------|-----------------------|--------------------------|
| Ni 231.604 | 0.0001 | 2.990 | 3.00 | 1.9 |
| Cr 267.716 | 0.0002 | 0.262 | 0.26 | 2.4 |
| Mn 257.610 | 0.00002 | 0.695 | 0.70 | 2.2 |
| Si 251.611 | 0.0003 | 0.234 | 0.24 | 3.5 |
| Cu 324.754 | 0.00004 | 0.085 | 0.09 | 2.2 |

*The RSD was calculated based on ten measurements for each element.

Certified by Arun Technology (<http://aruntechnology.co.uk/>).

For the determination of the detection limit values, the ICP-AES optimum operating conditions for each element analyzed were used (See Table 3). The blank solution was used to determine the background standard deviation. The standard deviation for the background signal was calculated for ten repeated measurements.

The detection limit values were calculated by the following formula:

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$$DL = (3 * SDIbl / IStd) * CStd$$

where:

DL = Detection limit.

SDIBL = Standard deviation of the intensity of the blank solution.

IStd = Background corrected net intensity of the standard.

CStd = The concentration of the analyte in the standard solution.

A detection limit of 0.0001% for Ni, 0.0002% for Cr, 0.00002% for Mn, 0.0003% for Si and 0.00004% for Cu were achieved in this study.

It is obvious from the results presented in Table (4), that measured concentrations for the five elements analyzed using ICP – AES are in a good agreement with the certified values for the reference standard Nickel alloy steel BCS 222 used in this study. Looking at the analytical results in table (4), It can be suggested that ICP – AES with the good capabilities this technique can offer such as good linear dynamic range, detection limit, precision and accuracy can prove to be a very valuable analytical technique used by the steel industry for both process and quality control of steel products.

Conclusion

Nickel-Steel alloy is one of the most important types of steel alloys due to its use in various places all around the world such as making storage cylinders for liquefied gases, heavy forgings, turbine blades, highly stressed screws, bolts, nuts, making shafts, gears, propeller shafts, and keys. The concentrations of the constituent elements for Nickel Steel Alloys were determined using ICP-AES with Meinhard nebulizer and Scott – Fassel double pass spray chamber. Analytical results achieved for Nickel 231.604 nm, Chromium 267.716 nm, Manganese 257.610 nm, Silicon 251.611 nm and Copper 324.754 nm show that concentrations obtained are in line with those for the reference

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standard used. A detection limit in the range of 0.00004 – 0.0003 wt% and RSDs of 1.9 – 3.5 % were achieved for the elements analyzed in this study. Based on the wide linear dynamic range, good detection limits, high accuracy and precision achieved, it can be suggested that this technique can prove to be a very valuable analytical technique used by the steel industry for both process and quality control of steel products.

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