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Study of Spectral Interferences and Line Selection for Steel Analysis Using Inductively Coupled Plasma Atomic Emission Spectrometry ICP-AES

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Quality Assurance Manager-Ministry of Higher Education and Scientific Research

Abstract

This paper is devoted to spectral interference studies and line selection for Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) when a low resolution spectrometer ($\Delta\lambda$ min = 2 Å) is used for steel analysis. It has been identified that some of the most intense lines for Cobalt, Zirconium, Lead, Nickel, Niobium and Molybdenum at low resolution cannot be used owing to spectral interferences. Different interference free lines for Cobalt, Chromium, Vanadium, Nickel, Molybdenum and Manganese have therefore been selected. The possibility of differentiating different types of steel by recording their spectrum at particular regions of wavelength corresponding to their elemental composition has also been demonstrated in this paper.

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دراسة التداخلات الطيفية واختيار الخطوط الرنينية لتحليل الفولاذ باستخدام تقنية مطيافية الانبعاث الذري /بلازما الحث المقترن AES – ICP

خالد شناوة زيارة

قسم ضمان الجودة ـ وزارة التعليم العالي والبحث العلمي

الخلاصة

يركز هذا البحث على دراسة التداخلات الطيفية واختيار الخطوط الرنينية لتحليل مادة الفولاذ باستخدام مطيافية الانبعاث الذري /بلازما الحث المقترن (ICP – AES) وبمطياف ضعيف الفصل والتمييز ($\Delta\lambda$ min = 2 Å) حيث وجدت الدراسة بان بعض الخطوط االرنينية القوية لكل من عناصر الكوبلت Co والزركونيوم Zr والرصاص Pb والنيكل Ni والنيوبيوم Nb والمولبدينوم Mo لا يمكن استخدامها بسبب التداخلات الطيفية. لذلك تم اختيار خطوط رنينية اخرى خالية من التداخلات لكل من عناصر الكوبلت Co والكروم Cr والفناديوم V والنيكل Ni والمولبدينوم Mo والمنغنيز Mn. كذلك تناول البحث امكانية تمييز انواع مختلفة من الفولاذ بناءا على مكوناتها من العناصر من خلال تسجيل الطيف في مناطق محددة من الاطوال الموجية.

الكلمات المفتاحية: التداخلات الطيفية ، مطيافية الانبعاث الذري AES ، بلازما الحث المقترن ICP ، تحليل الفولاذ ، مطياف ضعيف الفصل والتمييز.

Introduction

Spectral line interferences occur when a line of interest cannot be easily resolved from a line of another element or from a molecular band [1]. Spectral interferences can be common in high temperature plasmas as opposed to flame-based systems given the complete excitation and subsequent emission of all compounds in the sample (including the argon). With the use of inductively coupled plasma atomic emission spectrometry ICP – AES (temperature ~ 6000 to 10 000 K) as an analytical technique [2 – 9] , nearly every species that exists in the plasma is caused to emit light, therefore a considerable number of spectral lines are generated. As a result, the choice of spectral line for determining a trace element becomes dependent on the relative freedom from other spectral features at that wavelength. Therefore, a knowledge of

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the spectral interferences, particularly in the use of a low resolution spectrometer is an important factor for the most efficient use of low resolution spectrometers in analytical AES.

The severity of interferences for two spectral lines is expressed in terms of Rayleigh criterion [10, 11]. For two lines of equal intensity, the Rayleigh criterion states that the lines are resolved if the depth of the valley between the peaks is at least 19% of the peak height. Direct overlap occurs if the Rayleigh criterion is not met, and assuming the lines are inherently broad, no amount of resolving power can alleviate this type of interferences. In a closely similar situation, there may actually be some wavelength separation between two lines, but the dispersing apparatus may not be adequate for the isolation of the analyte line. Overlap again occurs but it is instrument dependents [10].

If the wavelength separation between two lines exceeds the Rayleigh criterion, isolation of the analyte may be provided if an optical system with adequate dispersion is used [11]. A common means of rating the dispersing ability of resolving power of the spectrometer is through the calculation of its spectral bandpass (SBP) [11].

Spectral Bandpass (SBP) = Slit Width x Reciprocal Linear Dispersion (RLD)

High resolution instruments provide an (SBP) between 0.001 and 0.01 nm. Medium resolution spectrometers have an (SBP) in the range of 0.01 – 0.1 nm. The lower the SBP, the more likely it is that closely spaced lines are separated [11].

A spectrometer with a significantly narrow (SBP) is a definite asset for performing analysis. There is, however, a limit to the effectiveness of the best optical instruments. This limit is determined by broadening of the lines in the plasma [12, 13].

Stray light [14] is radiation that reaches a detector unintentionally. The main source of stray light are reflections and optical imperfections associated with the optical components which can contribute to stray light. There are several ways to reduce stray light in spectrometers: use a holographic grating, paint the interior of the instrument with matt black paint, insert baffles to obstruct radiation from all except the axial direction, and enclose the photomultiplier in a suitable housing so that only light passing through an exit slit can reach the photocathode.

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Sample Preparation

2.5 gram of Leaded steel, high speed steel, high Silicon steel, Carbon steel and Nickel steel have been accurately weighed individually in a microbalance and dissolved in 50 ml of 1:1 HNO3 and HCl mixture. The mixture was heated for five minutes until the steel dissolved and after that the sample was filtered using filter paper and diluted to 250 ml using distilled water.

Instrumentation

ICP – AES with Meinhard nebulizer [15, 16] and double pass spray chamber [17] 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 kΩ load across the input to act as a current to voltage convertor. Table (1) describes the instrumentation used with the operating conditions listed at Table (2).

Table (1): The Instrumentation Used

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). Reciprocal linear dispersion 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	
Nebulizer	Meinhard Nebulizer
Spray Chamber	Scott – Fassel double pass spray chamber.

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Table (2): Operating Conditions and Parameters for Spectral Interference Studies Using ICP – AES

Forward Power	1 KW
Viewing Height	15 mm a.l.c
Coolant Gas Flow Rate	12 L/min Ar
Injector Gas Flow Rate	0.8 L/min Ar
Auxiliary Gas Flow Rate	0.4 L/min Ar
PMT Voltage	1000 V
Entrance and Exit Slit Width	
Low Resolution	0.5 mm
High Resolution	0.02 mm
Reciprocal Linear Dispersion	0.4 nm/mm

Results and Discussion

These studies are concerned with characterizing the emission spectrum of different kinds of steels (compositions of these steels are shown in Table 3) to identify potential spectral interferences within the bandpass of the low resolution spectrometer ($\Delta\lambda$ min = 2 Å). The high ($\Delta\lambda$ min = 0.08 Å) and low ($\Delta\lambda$ min = 2 Å) resolution requirements have been achieved by changing the slit width of the spectrometer (RLD = 4 Å / mm). Aqueous solutions of these steels have been analysed under the conditions listed in Table (2) using ICP – AES. From Figures (1– 5) it is clear that the most intense lines for Cobalt CoI 345.35 nm, Zirconium ZrII 349.62 nm, Lead PbI 405.78 nm and Niobium NbI 405.89 nm as well as some of the most intense lines for Nickel NiI 361.93 nm and Molybdenum MoI 379.82 nm which have been recorded at low and high resolution ICP – AES cannot be resolved within the range of 2Å spectral bandwidth.

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Table (3): The Composition of Steel Used

Steel Used	C%	Pb%	Si%	S%	P%	Mn%	W%	Cr%	V%	Mo%	Co%	Sn%	Ni%	Cu%	Al%	B%	Nb%	Zr%	Sb%
Leaded Steel BCS 212/1	0.36		0.23	0.03	0.027	0.91													
High Silicon Steel BCS 317	0.028		3.49		0.015	0.08													
High Speed Steel BCS 241/1	0.85		0.33	0.033	0.021	0.3	19.61	5.03	1.57	0.52	5.67	0.025							
Nickel Steel BCS 222	0.35		0.24	0.04	0.04	0.7		0.26					3.0	0.09					
Carbon Steel BCS 457/1	0.324	0.004	0.051	0.042	0.01	0.3			0.17		0.023				0.111	0.002	0.022	0.006	0.038
High Speed Steel 31B	0.71		0.31	0.008	0.021	0.31	17.98	4.09	1.19	0.5	4.98	0.01	0.31	0.1	0.006				

Figures (1– 5): High and low resolution spectra for steel solution samples recorded using (ICP – AES) at the operating conditions listed in Table(2) showing that some lines cannot be resolved using low resolution spectrometer. The bottom spectrum is for the blank.

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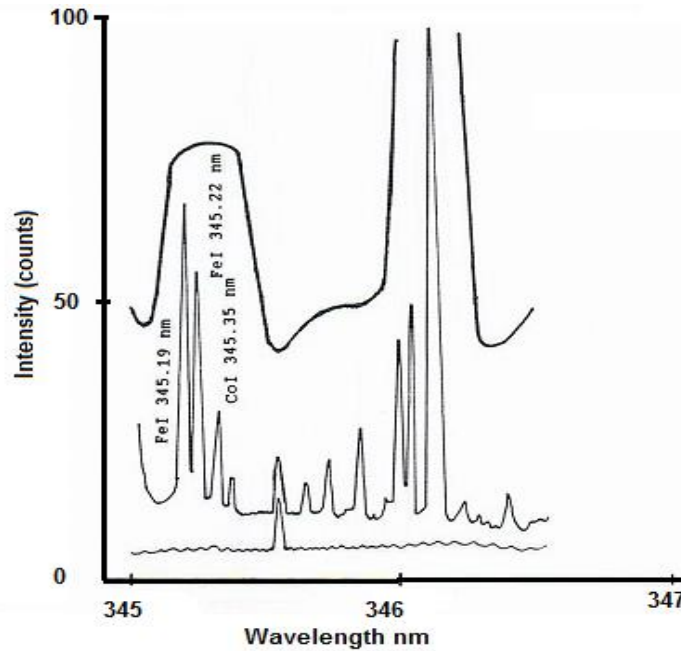
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Figure (1): Shows Upper Spectrum (2 Å spectral bandwidth) and Lower Spectrum (0.08 Å spectral bandwidth) for Cobalt CoI 345.35 nm line using carbon steel sample.
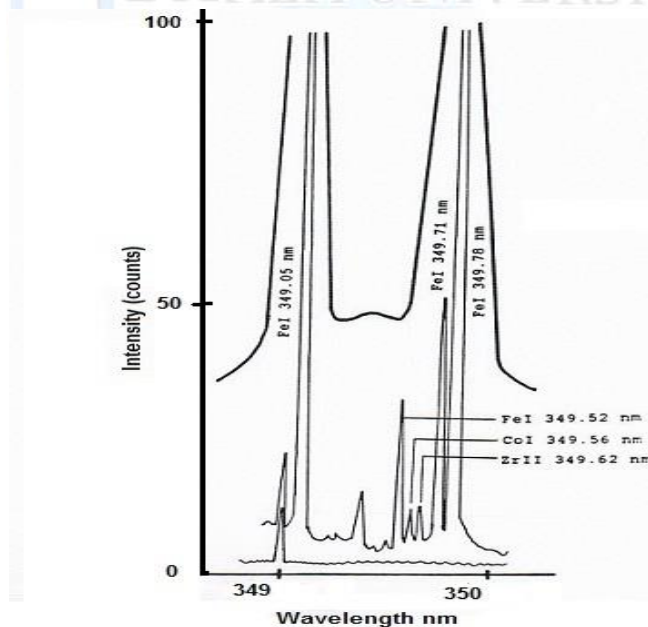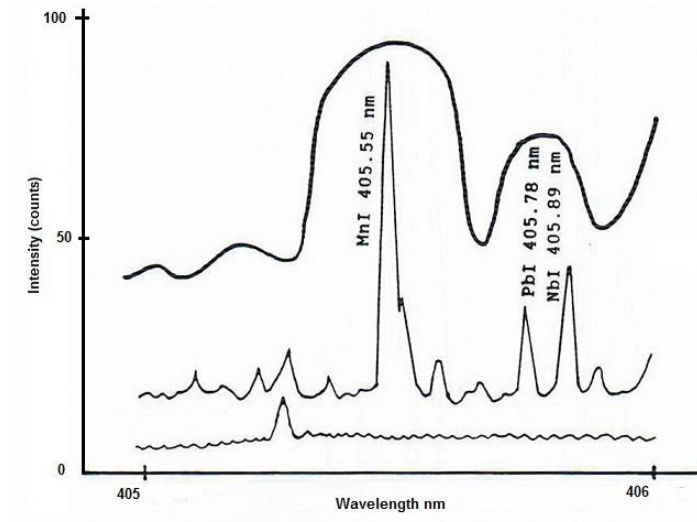

Figure (2): Shows Upper Spectrum (2 Å spectral bandwidth) and Lower Spectrum (0.08 Å spectral bandwidth) for Zirconium ZrII 349.62 nm line using carbon steel sample.

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Figure (3): Shows Upper Spectrum (2 Å spectral bandwidth) and Lower Spectrum (0.08 Å spectral bandwidth) for Lead PbI 405.78 nm and Niobium NbI 405.89 nm lines using carbon steel sample.
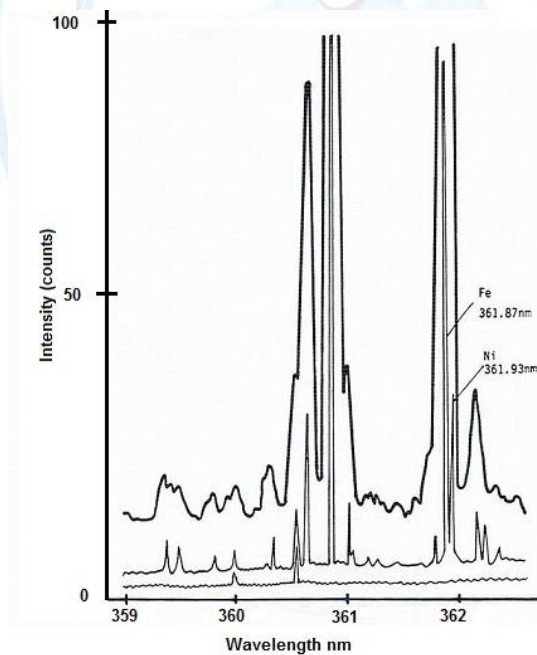

Figure (4): Shows Upper Spectrum (2 Å spectral bandwidth) and Lower Spectrum (0.08 Å spectral bandwidth) for Nickel NiI 361.93 nm line using carbon steel sample.

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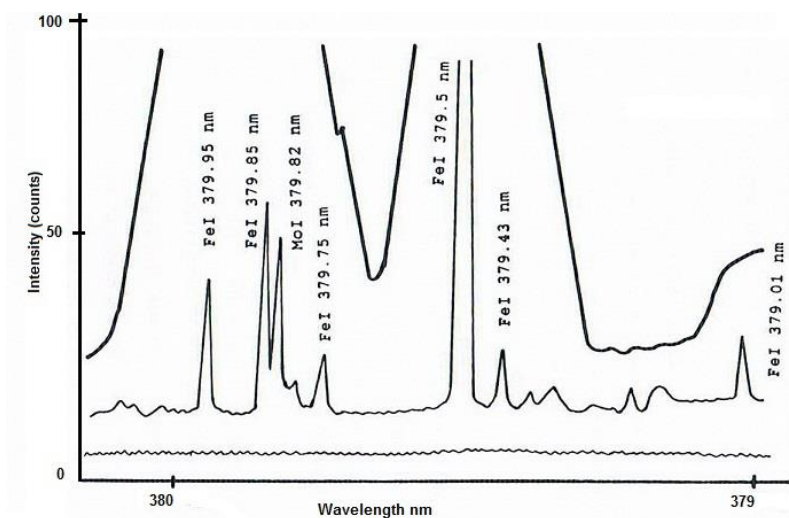
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Figure (5): Shows Upper Spectrum (2 Å spectral bandwidth) and Lower Spectrum (0.08 Å spectral bandwidth) for Molybdenum MoI 379.82 nm line using carbon steel sample.

Choosing an analytical line for the analysis of any element depends mainly on the relative intensity of that line and the freedom from any potential interferences. When spectral interferences have to be accounted for, the selection of the most desirable line depends on the sample type.

The best lines for the analysis of Chromium, Cobalt, Vanadium, Manganese and Aluminum have been selected [18] using ICP – AES at the operating conditions listed in Table (2). The spectrum for each of these lines has been recorded at high (0.08 Å) and low (2 Å) resolution by changing the slit widths of the spectrometer. The most intense lines for Chromium CrI 425.435 nm and Vanadium VI 437.924 nm have been found to be resolved in both high and low resolution without any interferences (See Figures 6 and 7). For the analysis of Manganese the MnI 403.076 nm which is the most intense line for Manganese has been selected to be the best line for the analysis of this element. The only expected interference is the NbI 403.252 nm line even with the second most intense line for Manganese, MnI 403.307 nm present (See Figure 8).

For the analysis of Cobalt, CoI 345.35 nm cannot be used as shown in Figure (1). Also, the second most intense line CoI 340.512 nm cannot be used because of the presence of a number

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of Iron lines. Therefore, the CoI 350.228 nm has been selected as the best line for the analysis of Cobalt in steel using a low resolution spectrometer (See Figure 9).

Figure (10) shows the AlI 396.152 nm, which is the most intense line for Aluminum, at both high and low resolution. The only expected to interfere with this line is the weak line for Titanium TiI 396.285 nm.

Figures (6 –10): High and low resolution spectra for steel solution samples recorded using (ICP – AES) at the operating conditions listed in Table (2) showing the lines which could be used using low resolution spectrometer. The bottom spectrum is for the blank.
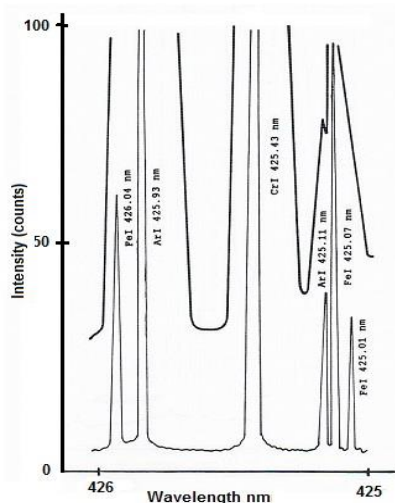

Figure (6): Shows Upper Spectrum (2 Å spectral bandwidth) and Lower Spectrum (0.08 Å spectral bandwidth) for the region of 425 – 426 nm for high speed steel solution sample.

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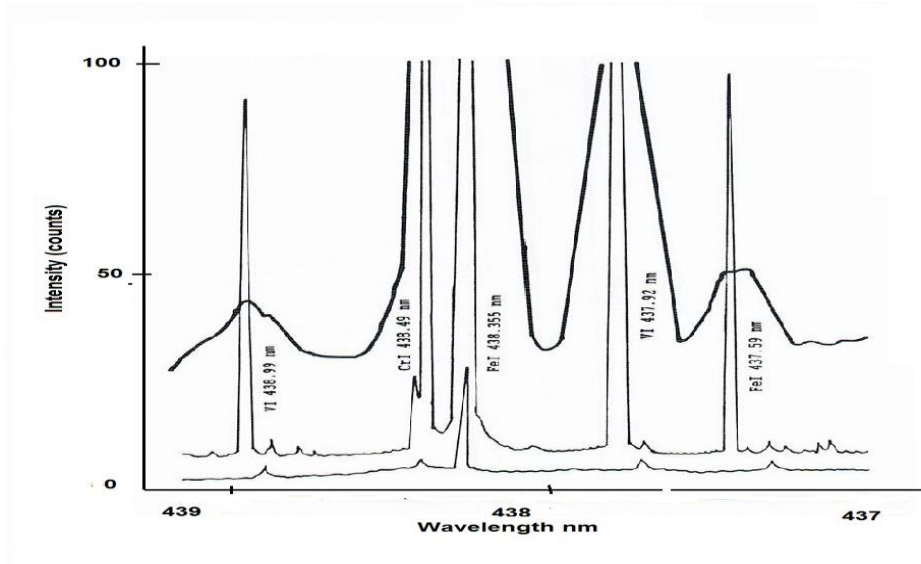
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Figure (7): Shows Upper Spectrum (2 Å spectral bandwidth) and Lower Spectrum (0.08 Å spectral bandwidth) for the region of 437 – 439 nm for high speed steel solution sample.
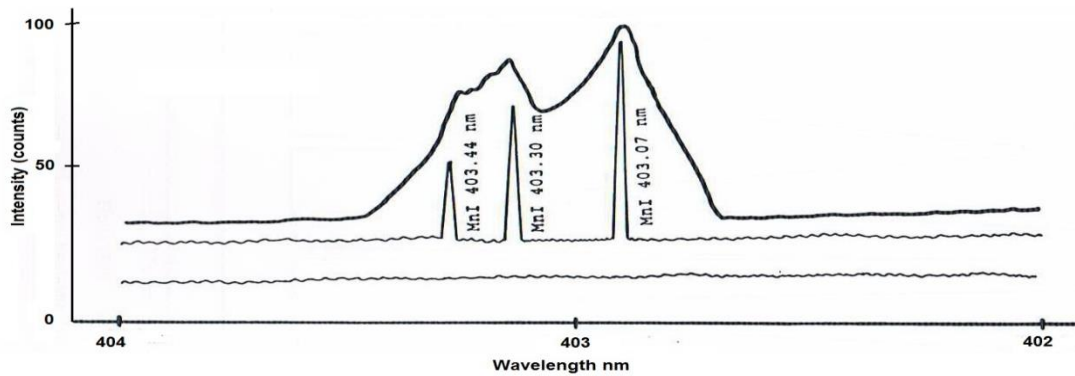

Figure (8): Shows Upper Spectrum (2 Å spectral bandwidth) and Lower Spectrum (0.08 Å spectral bandwidth) for the region of 402 – 404 nm for carbon steel solution sample.

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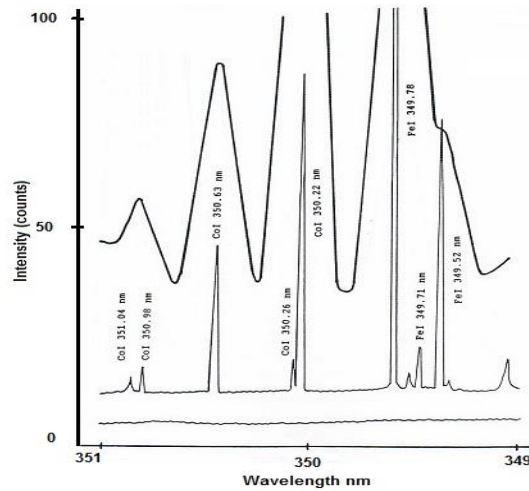
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Figure (9): Shows Upper Spectrum (2 Å spectral bandwidth) and Lower Spectrum (0.08 Å spectral bandwidth) for the region of 349 – 351 nm for high speed steel solution sample.
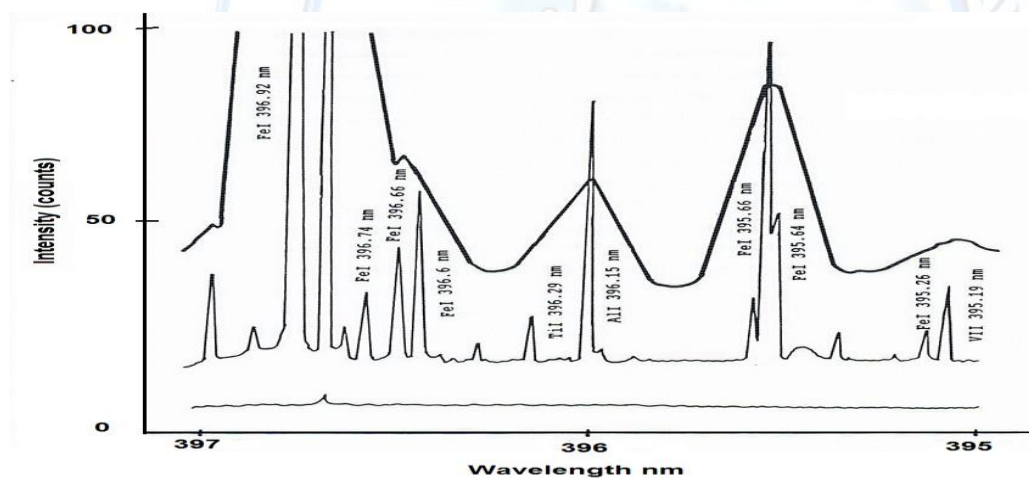

Figure (10): Shows Upper Spectrum (2 Å spectral bandwidth) and Lower Spectrum (0.08 Å spectral bandwidth) for the region of 395 – 397 nm for carbon steel solution sample.

It was thought that it would be possible to identify different steels by recording their spectra at a particular region of wavelength corresponding to their elemental composition.

Three kinds of steel; high speed steel BCS 241/1, leaded steel BCS 212/1, and high silicon steel BCS 317 have been used. The composition of these steels are listed in Table (3). The

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solutions of these samples prepared as described before and the instrumentation described in Table (1) was used.

To differentiate any kind of steel from another, two things must be taken into account. Firstly the composition of the steel is compared to others, secondly the identification of lines for elements which can be resolved with the low resolution spectrometer. For high speed steel which contains 5.03% Chromium, the CrI 425.435 nm which can be resolved with a 2 Å bandpass spectrometer has been selected. The spectrum for 425 – 426 nm has been recorded at both high and low resolution for these three kinds of steel (See Figures 6, 11 – 13). From these figures it is obvious that the high speed steel can easily be distinguished from the other two kinds.

The same thing has been done for these steels by recording their spectra at the region of 405 – 406 nm where the most intense line for Lead is at that region which might be used to differentiate the Leaded steel from the others. It is clear from these spectra (See Figure 14) that the lead line 405.783 nm is completely resolved at high resolution whereas it is not at low resolution because of the presence of some weak manganese lines (MnI 405.795 nm and MnI 405.89 nm).

From an examination of the elemental composition of these steels we found that there are three cases which might face the analyst if differentiation between any particular kind of steel from the others is required. In the first case like in the high speed steel, there is an element with an interference free line which can be used to differentiate this kind of steel from others. In the second case e.g. in the high leaded steel, there is an element which differentiates it from the others but without an interference free line at low resolution. And in the third case, like in the high Silicon steel, there are no elements to differentiate it from the others, but there is Silicon at different concentrations.

So by doing a multi – element analysis using the lines selected in this study for steel analysis and taking two things into account, the presence of elements and the concentration of these elements and by comparing that to tables that contain all kinds of steel with their elemental composition and their concentration, might help us in this issue.**Figures (11 – 14):** Spectra for solution steel samples recorded using ICP – AES at the operating conditions listed in Table

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(2) showing the possibility of differentiating some types of steel than others by recording their spectra at a particular wavelength region.
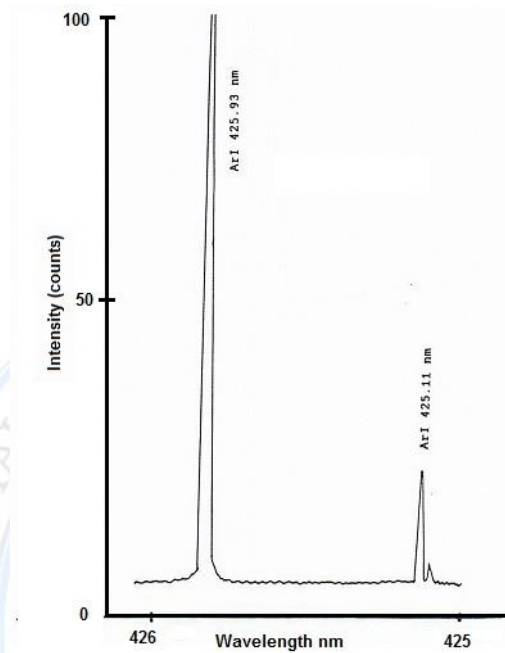

Figure (11): Shows the blank (50 ml of 1:1 HNO3 and HCl mixture diluted to 250 ml) spectrum for 425 – 426 nm region at 0.08 Å spectral bandwidth.
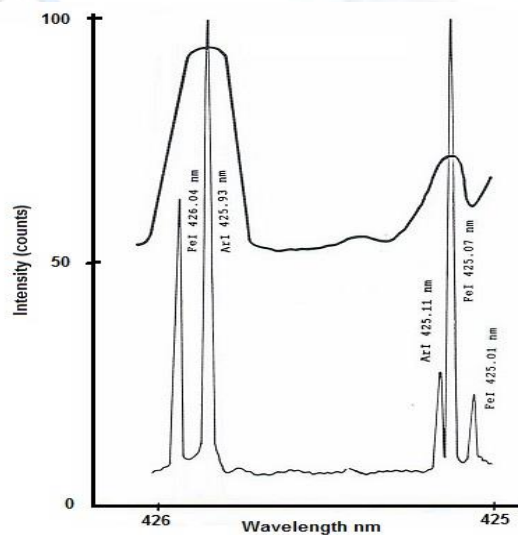

Figure (12): Shows Upper Spectrum (2 Å spectral bandwidth) and Lower Spectrum (0.08 Å spectral bandwidth) for the high Silicon steel sample.

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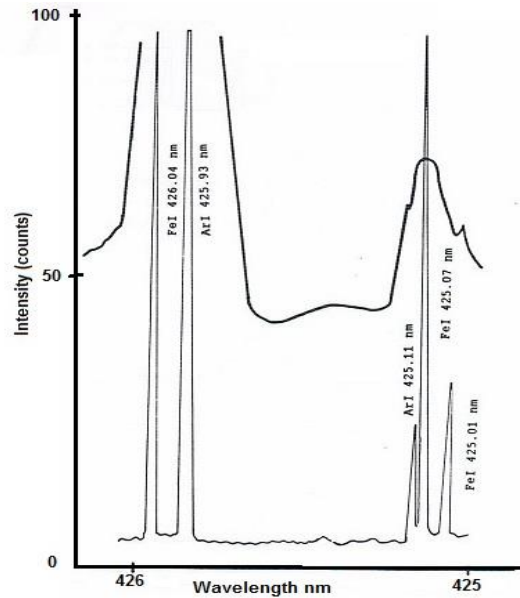Inductively Coupled Plasma Atomic Emission Spectrometry ICP-AES**

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**Figure (13): Shows Upper Spectrum (2 Å spectral bandwidth) and Lower Spectrum
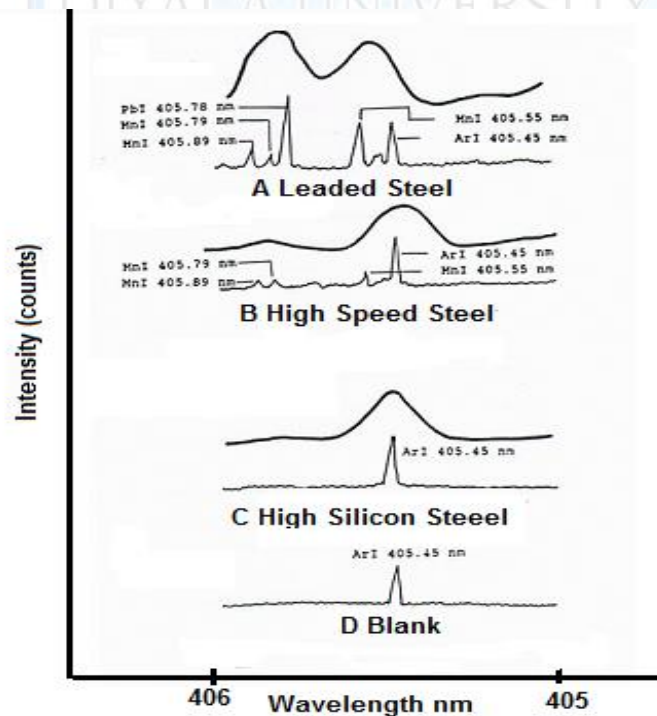(0.08 Å spectral bandwidth) for the Leaded steel sample.**

**Figure (14): Shows Upper Spectrum (2 Å spectral bandwidth) and Lower Spectrum
(0.08 Å spectral bandwidth) for (a) Leaded steel, (b) High speed steel, (c) High Silicon
steel sample and (d) The lower spectrum (0.08 Å spectral bandwidth) for the blank.**

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Conclusion

This publication is devoted to the spectral interferences faced for steel analysis when a low resolution (2 Å) spectrometer is used. Impossibility of using some of the most intense lines for Cobalt, Zirconium, Lead, Nickel and Molybdenum have been demonstrated by recording the spectrum of some kinds of steel at high and low resolution requirement by changing the slit width of the spectrometer using ICP – AES.

Different lines for the most important elements in the steel such as Cobalt, Chromium, Vanadium, Nickel, Molybdenum and Manganese have been selected to be used for the analysis of steel using low resolution spectrometer.

The possibility of differentiating any kind of steel from the others by recording their spectrum at a particular region of wavelength corresponding to their elemental composition has also been tried. Some problems might be faced in this case such as finding an element which differentiates any particular kind of steel but without free interferences line at the low resolution spectrometer or impossibility of finding any element which might be used for differentiating. These problems might be avoided by doing a multi – element analysis for steels and taking two things into account, these are, the presence of the element and the concentration of these elements, and by comparing that to special tables which contain all kinds of steels with their elemental composition and their concentration.

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