Quantitative colorimetric determination of Ni^{2+} metal ions using conventional and smart phone digital-imaging methods

1. Importance of the experiment:
Nickel is a transition element and commonly exists in +2 oxidation state, though +1, +3 and +4 states are also observed in nickel complexes. Nickel plays an important role in biological systems as a constituent of several enzymes. Nickel is also present in soils and plants, and its concentration varies widely from trace quantities to being a major constituent. Therefore, determination of nickel at different concentration levels in variety of samples becomes very important.

2. Nickel Toxicity: Compared with other transition metals, Nickel is a moderately toxic element. However, it is known that inhalation of nickel and its compounds can lead to serious problems, including cancer in the respiratory system. Moreover, Nickel can cause a skin disorder known as nickel-eczema (10.1016/j.kijoms.2016.08.003).

3. Nickel in Industries: A thin layer of nickel onto a metal object can be decorative, provide corrosion resistance, wear resistance, or used to build up worn or undersized parts for salvage purposes. Nickel alloys are used extensively because of their corrosion resistance, high temperature strength and special magnetic and thermal expansion properties.
The major alloy types that are used are:

- Iron-Nickel-Chromium alloys
- Stainless Steels
- Copper-Nickel alloys and Nickel-Copper alloys
- Nickel-Chromium Alloys
- Nickel-Chromium-Iron alloys
- Low Expansion Alloys
- Magnetic Alloys (http://www.nickel-alloys.net/nickelalloys.html)

Expt. No.: **Date:**

Experiment	**Quantitative colorimetric determination of Ni^{2+} metal ions using conventional and smart phone digital-imaging methods**
Problem definition	Corrosion protection in steel depends on the amount of Ni (acts as passivating metal) in its composition. Hence, it is important to analyze the amount of Ni in steel for its use in industry.
Methodology	Ni-DMG forms a stable colored complex. With increasing concentration of Ni in solution, its color intensity also increases. In turn, the color intensity is a function of color coordinates (Red, Blue and Green, RGB) in the image taken using mobile phone camera.
Solution	Estimation of Ni concentration in the unknown sample from the calibration graph plotted based on different known Ni concentrations.
Student learning outcomes	Students will learn to perform colorimetric method, perform RGB response analysis and analyze Ni composition in different grades of steel

(i). Principle:

(a). Colorimetric method:

Photo-sensitive measurements are expressed in terms of absorbance, *(A)* as given in Eq. (1). Further, the linear relationship between absorbance (A) and concentration of the analyte

$$\varepsilon cl = A = \log(I_0/I) \quad \ldots (1)$$

Where, I_0 is the incident light power, I the transmitted light power, ε = molar absorptivity, c = concentration of analyte and l = thickness of the solution.

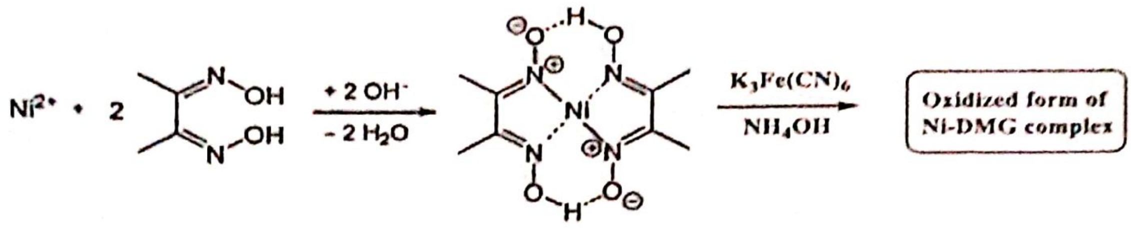
(b). Digital-imaging method:

The color and intensity of digital image are usually 24 bit data (8 bit R + 8 bit G + 8 bit B) forming an additive color space, in which R, G and B lights are added together in various combinations to reproduce a broad range of colors. By using combination of R, G and B intensities, many colors can be displayed. The intensity of each color has 256 levels (from 0 to 255). The value of R = 0, G = 0, B = 0 refers to pure black while R = 255, G = 255, B = 255 is pure white. With this system, unique combinations of R, G and B values are allowed, providing for millions of different hue, saturation and lightness shades. These extensive dynamic colors of images provide the database for quantitative analysis. The goal of this study is to employ digital images-based colorimetry for the determination of Ni^{2+} concentration in aqueous samples.

The concentration of analyte is a function of color coordinates: $c = RGB$ ... (2)

(ii) Scheme of the reaction and requirements

Dimethylglyoxime (DMG) reacts with Ni^{2+} to form a pink-colored $Ni(dmg)_2$ complex in alkaline medium. It gets oxidized by potassium ferricyanide ($K_3[Fe(CN)_6]$) in alkaline medium to form a brown-red, water soluble oxidized $Ni(dmg)_2$ complex (**Scheme 1**).



Scheme - 1

Absorption spectrum of the oxidized complex shows absorption maxima at a wavelength of 440 nm (**Fig. 1**). Concentration of Ni^{2+} in the given unknown sample is determined from the calibration graph (**Fig. 2**).

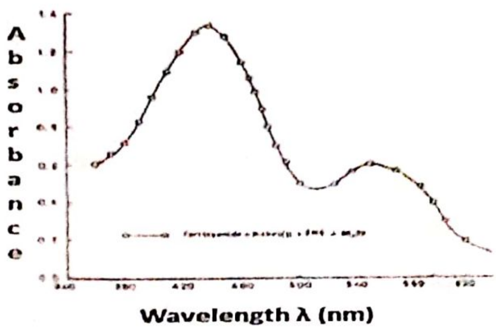


Fig. 1: Absorption spectrum of oxidized Ni(II)-DMG complex showing λ_{max} at 440 nm

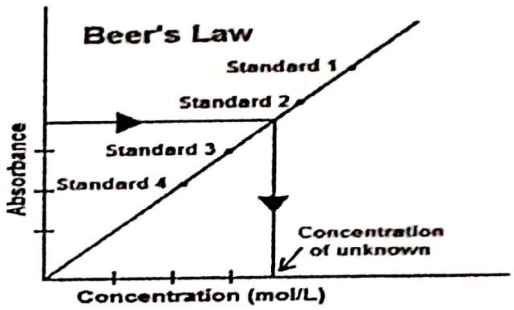


Fig. 2: Model calibration curve for Ni(II) determination

Requirements:

Reagents and solutions: $NiSO_4$ (100 ppm), NaOH (1 N) solution, DMG, $K_3[Fe(CN)_6]$

Instrument: Colorimetry and smartphone

(iii). Procedure:

(a). Colorimetry method: Take 5 standard 50 mL volumetric flasks (to prepare 4 known and 1 unknown solution). Fill the burette with Ni stock solution (100 ppm). Add 1, 2, 3 and 4 mL of the Ni solution in burette to the std. flasks to get 2, 4, 6 and 8 ppm of steel containing nickel(II) solutions. The unknown sample will be furnished in another 50 ml volumetric flask. Further, add 0.5 mL of DMG solution followed by 0.5 mL of $K_3[Fe(CN)_6]$ solution using a burette to all the 5 std. flasks. All the flasks are shaken well once and waited for 5 minutes. After that, make up the 50 mL mark in std. flask with 1N NaOH solution. Allow the flasks at least 10 minutes for the complete complex formation. Absorbance of the formed brown-red solution is measured at 440 nm against NaOH solution (blank). Record these absorbance readings in **Table 1**.

Draw a calibration graph taking concentration of Ni^{2+} (in ppm) as X-axis and absorbance readings as Y-axis. A straight line that passes through the origin (see **Fig. 2**) is an indication that the measured data obeys Beer's Law. From the calibration plot, measure the concentration of nickel in the given unknown sample.

(b). Digital imaging method: The prepared standard solutions are lined up along with unknown concentration sample and blank. Using a white paper as background, take a photograph of the samples by holding the camera around 50 cm away. Calibration curve will be constructed through the RGB values of analytical response with different conc. of Ni^{2+} ions using "RGB Tool" APP. In the plotted graph, RGB response varies linearly *vs* the analyte concentration. In order to get precise analysis, follow the steps given below:

Transfer prepared standard solution and unknown solution
into different colorimetric test tubes

↓

Take image of all test tube solution
using smart phone camera

↓

Open the image processing app

↓

Go to gallery, open the image stored in app and
extract RGB values for each image/conc.

↓

Process the RGB values (R/G) or (R/B) or (G/B)
etc., till to get linear response

↓

Plot the calibration curve using RGB linear
response vs concentration

↓

Find the unknown conc using the
calibration curve

Table 1: Experimental Data

	Data collected from Colorimetric device		Data collected from smartphone device*				
S. No.	Conc (ppm)	Abs (Y- axis)	R	G	B	G/B	B/G
1.	2	0·110	172	147	125	1.176	0·85
2.	4	0·193	142	115	96	1·198	0·834
3.	6	0·311	110	87	68	1·279	0·781
4.	8	0040	80	56	38	1·474	0·679
5.							
	Unknown	0·26	120	100	75	1·333	0·75

*If your solution looks Red or blue or green, then the corresponding ratio can be ignored and select RGB data which is linear with concentration of analyte for plotting calibration graph (Y-axis)

Result:

(i). Concentration of Ni in steel sample (using colorimetry) = 5.1 ppm (mg/L)

(ii). Concentration of Ni in steel sample (using digital imaging) = 4.9 ppm (mg/L)

Evaluation of result:

Sample number	Experimental value (ppm)	Actual value (ppm)	Percentage of error	**Least error % value**	**Marks awarded**
	Colorimetry method			0.5% error	
	Digital-imaging method				

X axis – conc. in ppm

Y axis – absolute value