Development of Microcontroller Based Two Channel Colorimeter for the Analysis of Cobalt in Water

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***Abstract*- An automated colorimeter equipped with different colored light-emitting diodes (LED) and two photodiodes (PD) as light source and detector, respectively, was developed. The intensity of LED was controlled by software managed pulse width modulator. Separate LEDs were used for the sample and reference cells. The light from sample or reference cell was detected by photodiode. The detected signal was fed to a PIC microcontroller through signal conditioning circuit. Neither monochromator nor wavelength selective filter was necessary, because color-LED produces mono-colored light. The analog signal from photodiode was converted into digital signal by on-chip multichannel analog to digital convertor. Absorbance of the sample solution was calculated relative to the reference one. Software program was written for the automatic determination of concentration of unknown species. The colorimeter was successfully used for the determination of concentration of cobalt in water.**

Keywords- colorimeter; light-emitting diode; photodiode; analog to digital convertor; cobalt.

I. INTRODUCTION

Molecules contain electrons in bound state which are excited to higher energy levels by the absorption of radiation of specific wavelength. Electrons in a molecule can be classified by the nature of chemical bond [1]. Electrons with an σ and pi bonds are excited by the radiation of shorter and longer wavelengths respectively. As the electrons in pi bond are more delocalized, they require relatively low intensity of light energy for the excitation. The electrons attached to atoms such as Cl, O or N as lone pairs are excited by low energy and longer wavelength radiation [2]. The photoelectric colorimeter is commonly used to measure the absorption of radiation by the molecules of analyte in a solution at different wavelengths and intensity of light.

Cobalt is an element that occurs naturally in the environment in air, water, and soil [3]. It is beneficial for living beings as it is a part of vitamin B_{12} [4]. It is used in the treatment of anaemia, because it stimulates the production of red blood cells. However, too high amount of cobalt may cause heart and thyroid problems [5]. It has been predicted that cobalt compounds are possibly carcinogenic to humans [6, 7]. Therefore, it is essential to measure the concentration of cobalt in water solution [8]. The modern automated photoelectric colorimeter is a simple device for the measurement of cobalt. Microcontroller (μC) is an essential part of such automated equipments, where it automates the process of measurement and control [9], and minimizes the manual operations.

The aims of the present work were (i) to design and construct electronic circuit of the PIC μC based photoelectric colorimeter, and (ii) development of software for the control and measurement of the incident and transmitted light respectively, determination of characteristics wavelength and absorptivity coefficient, calculation of absorbance and concentration. The rest of the paper is organized as follows: The method of photoelectric analysis is discussed in section II and design of electronic circuit and its description are discussed in section III. The steps in software development are discussed in section IV. The results are discussed in section V. Finally, the conclusions and future scope are discussed in section VI.

II. METHOD

The Beer and Lambert Laws [10] are based on the experimental results which describe the relationship between the absorption of light and concentration. Beer's Law states that absorption of light is proportional to the concentration of a species, while the Lambert's Law describes the relationship between path length and absorption. The combined Beer-Lambert Law can be written in terms of the proportion of light transmission.

$$T(\lambda) = \frac{I}{I_0} = 10^{-\varepsilon dc} \qquad (1)$$

Where T(λ) is the light transmitted through chemical species, I is the intensity of light emerging from the chemical species, I_0 is the intensity of incident light, ε is the molar absorptivity coefficient, d is the optical path length, and C is the concentration of absorbing species [11]. Absorbance can be obtained by taking logarithm on both sides of (1).

$$-\log_{10} T = A(\lambda) = \varepsilon dC \qquad (2)$$

Colorimeters are used to measure T(λ), and then concentration is obtained from (2). To produce the transmittance signal which is inversely proportional to the concentration of an analyte, a chemical reagent must be reacted with the analyte to form a product.

Analyte + Matrix + Reagent = Product + Matrix

An analyte is the species to be measured and the matrix is any chemical solution such as water which does not participate in the chemical reaction. The reaction forms a product which is directly proportional to the concentration and has a molar

absorptivity coefficient distinct from both the reagent and analyte. An ideal reagent is one, which does not absorb light. However, in practice, it absorbs the light and introduces error in the measurement. The error can be experimentally nullified by measuring concentration relative to the no-analyte blank solution. Error nullification can be achieved by using two cells, one for the blank and other for the sample.

A series of light absorption measurements are taken for the chemical product of known concentrations. From this data, a calibration curve is generated which is used to determine unknown concentration of analyte in a solution.

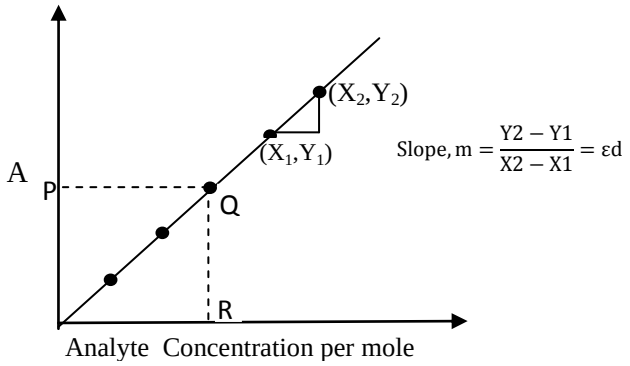

Fig. 1. A standard calibration curve for the absorbance (A) verses known concentrations of analyte.

To use the Beer Lambert Law for colorimetry, light absorption measurements are related to the analyte concentration using a standard calibration curve (see Fig. 1).

The light absorption caused by the reagent is first eliminated from the instrument.

The calibration curve is used to find the unknown concentrations of analyte. The point Q on the curve has co-ordinates (R,P). Where P is the measured value of absorbance, and R is obtained from the curve. The value of R gives the concentration.

The linear curve as shown in Fig 1. The equation 2 can be compared with the equation of line,

$$y = (mx) + b$$

gives,

$$A(\lambda) = (\varepsilon(\lambda)dC) + \text{error}$$

The grouped term $(\varepsilon(\lambda)d)$ is dependent on the optical path length of instrument and molar absorptivity coefficient of the chemical product being measured and has a fixed value for a particular analyte. Error in the calibration curve is the aggregate error of instrument and chemical reaction that results in a non-zero light absorption measurement for a zero analyte concentration.

III. CIRCUIT DIAGRAM AND DESCRIPTION

The function of colorimeter is to measure the amount of monochromatic light absorbed by a chemical species in the solution. There are three basic components for any colorimeter; a light source, sample cells, and light detector (see Fig. 2).

Group of LEDs work as light source. Photodiode measures light intensity leaving the cell as an electric current which is then processed by signal processor to determine absorbance and concentration.

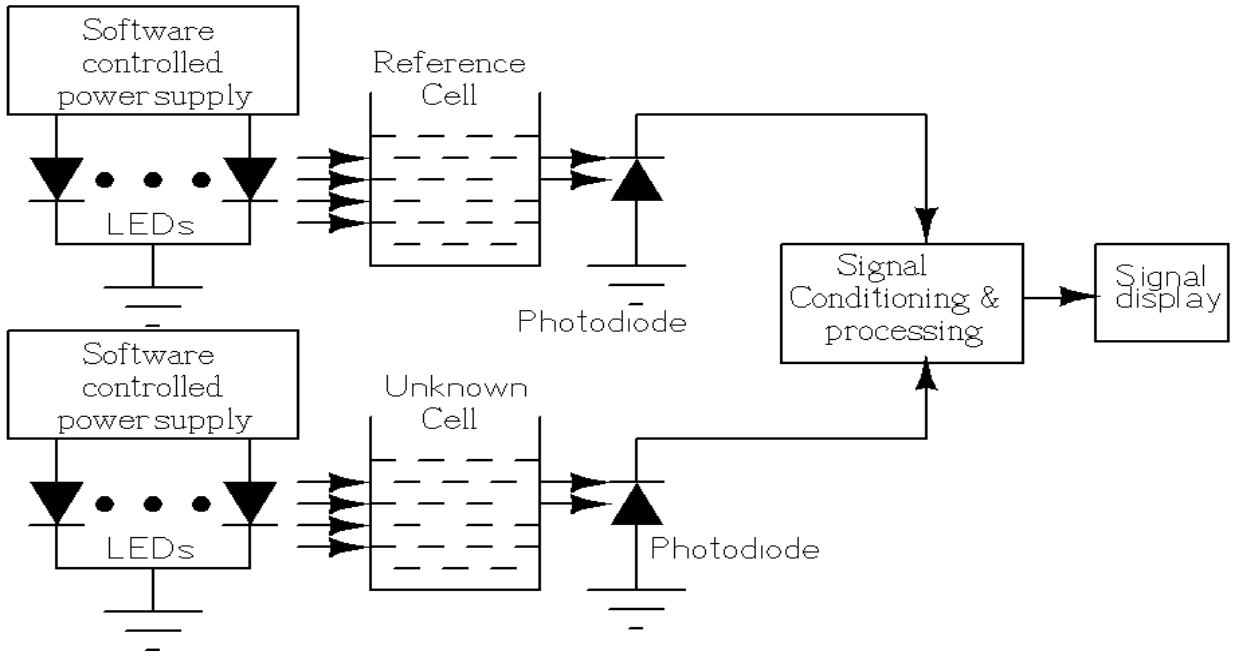

Fig. 2. Basic components of a colorimeter.

Colorimeter uses a monochromatic light source which is obtained by using a narrow spectrum light emitting diode (LED) [12]. Photodiode is used as a light detector. It generates a current proportional to the light intensity. Most measurement applications involve use of trans-impedance amplifier to convert the photodiode current into voltage [13]. Fig. 3 includes the schematic diagram of trans-impedance amplifier. In this circuit photodiode operates in photovoltaic mode, where the Op-Amp keeps the voltage across the photodiode at 0 V. The photodiode gives a small current even if there is no light present. This 'dark current' increases with increase in reverse voltage across the photodiode. Ideally, all of the photodiode current flows through the feedback resistor of Fig. 3, generating an output voltage equal to the photodiode current multiplied by the feedback resistor. The light source and detector system should be matched so that the spectral intensity of the source matches the responsivity of the detector. Responsivity is defined as,

$$R(\lambda) = \frac{Ip}{P}$$

Where Ip is the detector photocurrent and P is the incident light power. The optical path length is the distance travelled by light through the solution before reaching the light detector, generally it is one cm. The detector is less sensitive to the low concentration solutions. Sensitivity can be improved by use of longer path length.

The experimental setup comprises of bright LED as a source, photodiode as detector, a quartz or glass cuvette for the sample solutions, signal conditioner, a PIC18F4550 µC and 16x2 LCD display. The important features of PIC18F4550 are multichannel 10-bit ADC, in-circuit system programming and USB interface.

A 16x2 LCD display is commonly used in µC based circuits. A 16x2 LCD means it can display 16 characters on one line and there are 2 such lines. It has two registers, namely, command and data. A LCD can be set in a particular mode with the help of command register. Data register works as a buffer for the ASCII code of data.

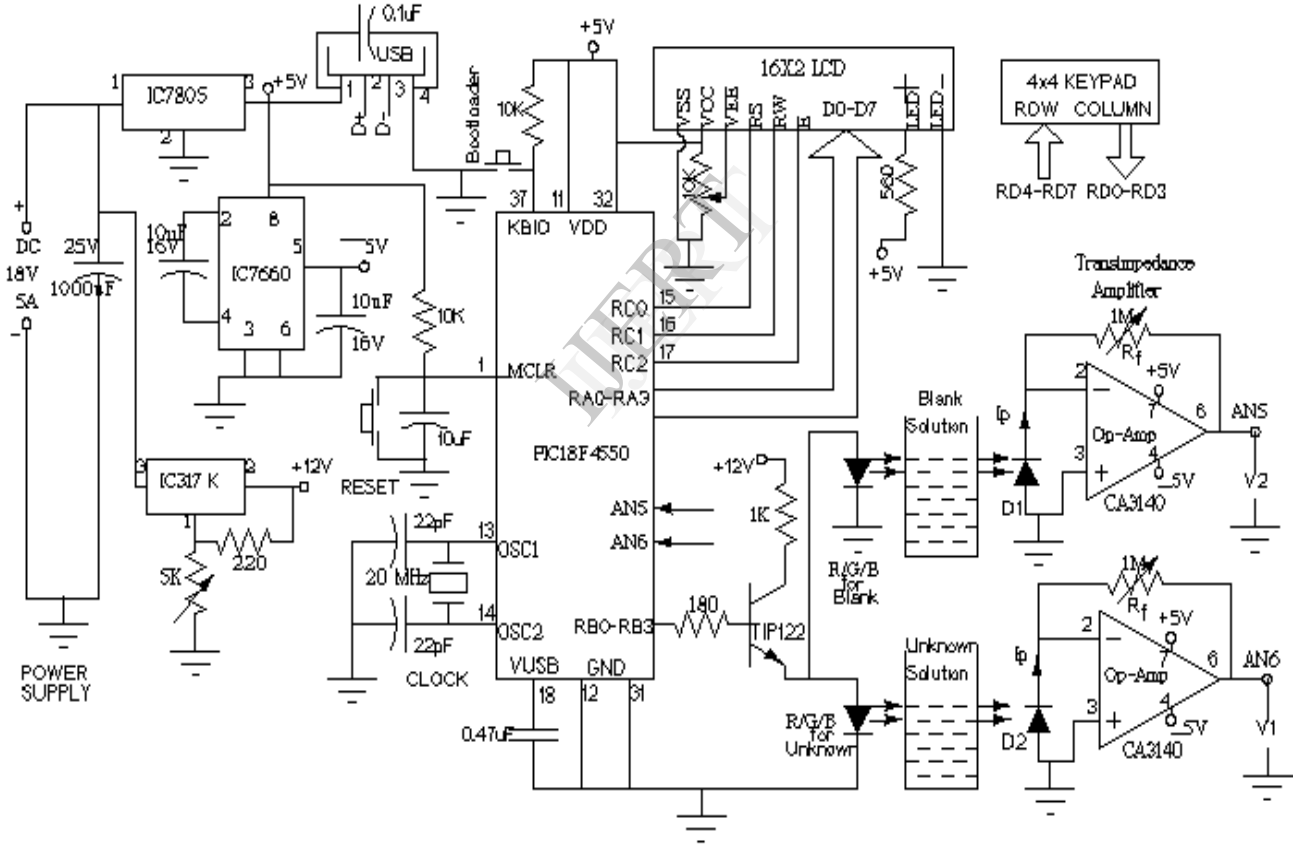

Fig. 3. Circuit diagram of PIC microcontroller based photoelectric colorimeter

IV. SOFTWARE DESIGN

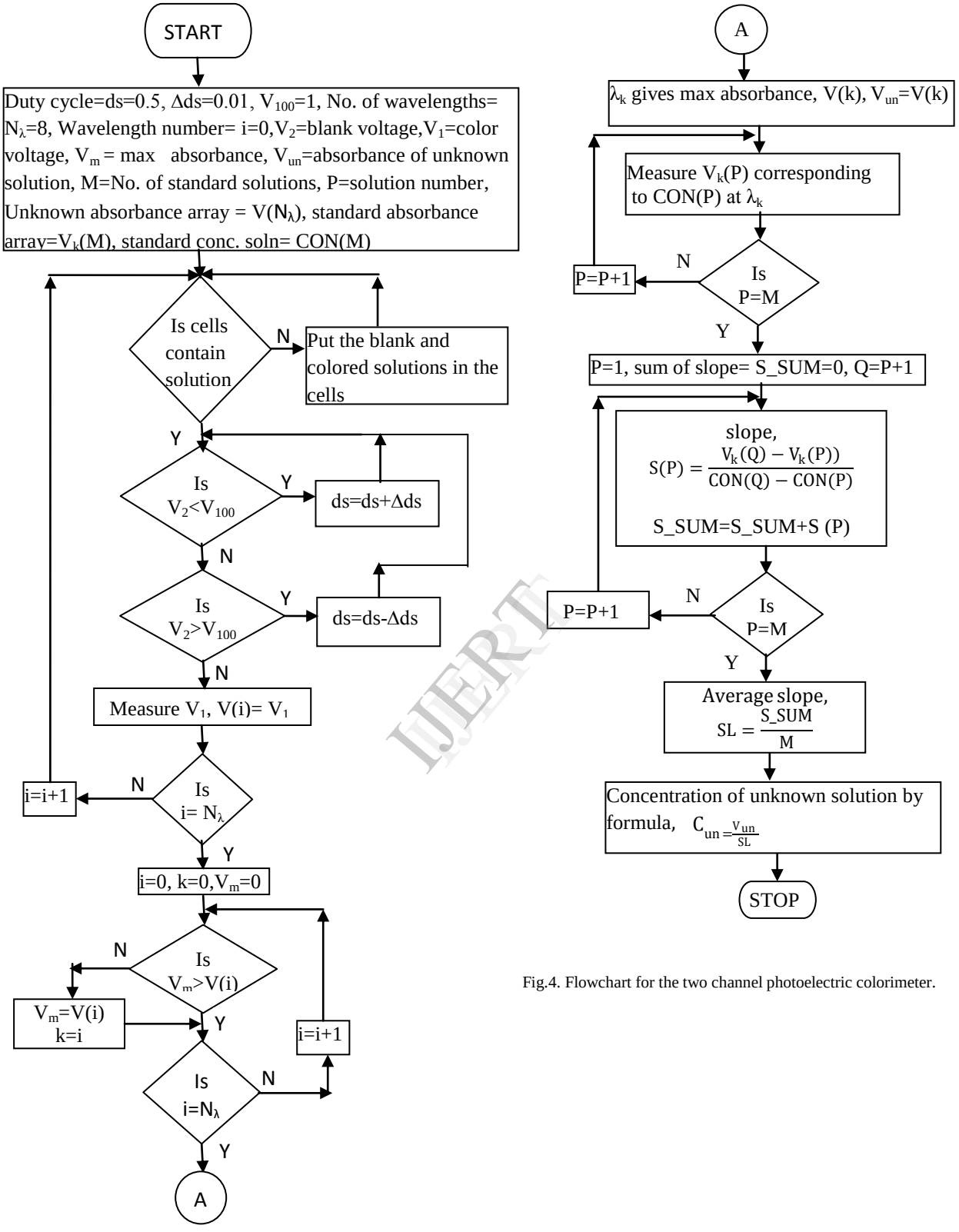

Fig.4. Flowchart for the two channel photoelectric colorimeter.

The software has been developed in MPLAB IDE and loaded into PIC18F4550 with the help of PIC KIT3 programmer. The flow chart depicted in Fig. 4 shows the sequence of steps involved in the analysis of chemical species. The software performs the functions: set the colorimeter for zero absorbance, detection of characteristics wavelength and identification of species, determination of calibration constant ε (λ)d and estimation of unknown concentration.

V. RESULTS AND DISCUSSION

The concentration of unknown species is determined from the calibration curve. In order to draw the curve, the first step is to find the maximum response wavelength λmax, and then in next step the absorbance values are measured for the series of known standard solutions. The values of absorbance for unknown solution at different wavelengths are depicted in Table I.

TABLE I. Absorbance by unknown concentration solution at different wavelengths

Wavelength, λ (nm)	Absorbance, A
400	0.27
420	0.42
470	0.50
500	0.63
530	0.53
620	0.12
660	0.11
700	0.09

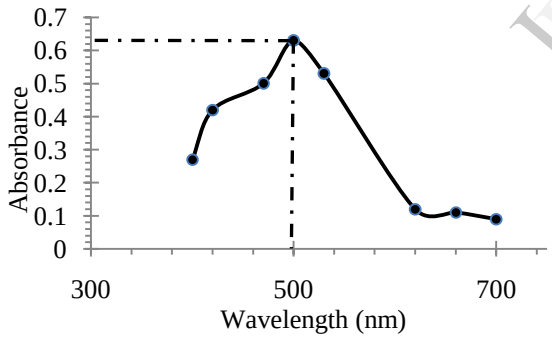

Fig.5. Wavelength vs Absorbance of unknown solution.

The plot of λ versus absorbance is shown in Figure 5. It is revealed from fig. 5 that the maximum response is at 500 nm, which is the wavelength of green colored light. The absorbance of various concentrations of Co^{2+} and unknown amount of cobalt in water are shown in Table II. Five different concentrations of Co^{2+} solutions were prepared. Using highest concentration solution of Co^{2+}, λ_{max} was determined and it was found to be 500 nm. At this λ_{max}, absorbance of different concentration solutions of Co^{2+} as well as unknown concentration solution of cobalt were measured and are depicted in the Table II. The graph of concentration verses absorbance is shown in Fig. 6.

TABLE II. Observations of absorbance for the known concentrations of Co^{2+} and unknown Co

ml of 0.2M $CoSO_4$ solution	Total Volume, ml	Concentration per M	Absorbance
5	25	0.04	0.11
10	25	0.08	0.30
15	25	0.12	0.36
20	25	0.16	0.57
25	25	0.20	0.63
Unknown Sample	25	Unknown Sample	0.40

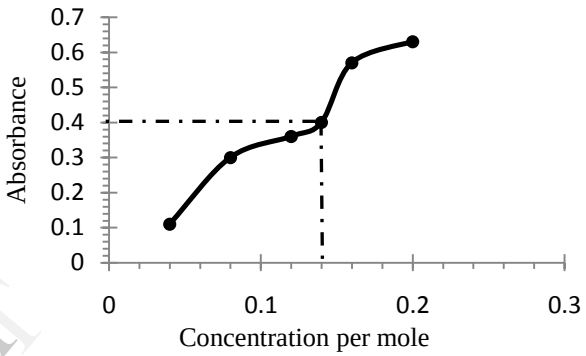

Fig. 6. Calibration curve for finding the unknown concentration of cobalt.

For a given unknown solution the measured absorbance is 0.40. The concentration of unknown solution is determined from the calibration curve as shown in Fig. 6. The value of unknown concentration of cobalt from the curve is found to be 0.141 M.

VI. CONCLUSIONS

The present work describes the two channel photoelectric color analyzer which uses two pairs of LED and photodiodes. One pair is used to convert the light transmitted by no-analyte blank solution into electric signal. This is used to eliminate the error introduced due to the absorption of radiation by reagent and the other pair is used for the unknown solution. The device is used as colorimeter by selecting the non-absorbing type reference solution. The developed device is cheap, portable, and easy to operate. It has been successfully used for the detection of cobalt in the water solution. The device can be used as a general purpose colorimeter, for the routine laboratory work.

Future scope: The software will be modified for the comparative study of pharmaceutical samples.

Limitations: The light transmittance data from colorimeter equipped with LEDs is less informative since the absorbance data is broken down per wavelength instead of one continuous absorbance output for all wavelengths of light.

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