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Analytical Tool for Determination of traces of Cu (II)

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Abstract
Heavy metals are widely existent in the contaminated environments. Copper is an essential metal for plants, microorganisms, animals and human beings to perform specific biological functions. As a toxicant at elevated levels of biologically available form, it produces a physiological response. Hence there is a need for rapid and sensitive methods for the analytical determination of copper. The aim of this article is to propose a rapid, selective and sensitive method for the determination of trace amounts copper (II). We aim to develop paptodes based on RGB analysis for copper determination and removal. A new optical analytical method, "digital RGB Analysis" is proposed instead of the conventional optical method, "spectrophotometry". MATLAB image processing tool can transform the color information into digital RGB values that can be treated as analytical information. The Paper optode has been prepared by immobilizing resorcinol and oxalic acid 1:1 solution on chromatographic (TLC) strip and heating for 15min at 80-90^{0}C. The obtained color pattern was analyzed using image processing tool of MATLAB software to determine copper (II). All parameters affecting intensity on optode have been optimized.
The proposed sensor was linear in the range 0.012-8.4µg mL^{-1} {12 µL of 1-700 µg mL^{-1}). The minimum detection limit was found 15ng mL^{-1}.The proportionality in intensity of the spot color on the optodes loaded with varying amounts of copper suggests its potential applications for environmental monitoring. The *paptode* can also be used for pollutant check at home. Thus the paper optode has great potential for this purpose.
Key Words: MATLAB, RGB analysis, Heavy metals, optical analytical method, TLC strip.

1. Introduction: Copper is an essential metal for plants, microorganisms, animals and human beings to perform specific biological functions. Copper is often added to fertilizers to serve as a supplement to plants. The failure to supply adequate amounts of copper leads to a variety of biochemical and physiological disorders in plants [1, 2]. In humans, it not only facilitates the conversion of iron to haemoglobin but also stimulates the growth of red blood cells. Copper is an integral part of certain digestive enzymes. Copper deficiency [3, 4] results in bodily weakness, digestive disturbances and impaired respiration. The effects of deficiencies vary depending on the nature of the living being, the factors affecting metal concentrations and the level of deficiency [5]. As a toxicant at elevated levels of biologically available form, it produces a physiological response. However, excess copper because of its potential incorporation in component organisms of food webs is of concern [6, 7]. Hence there is a need for rapid and sensitive methods for the analytical determination of copper. The determination of trace amount of copper has received considerable attention in the battle against environmental pollution. In the determination of copper various methods such as ICP-MS, ICP-AES, ion chromatography, anodic stripping analysis, FAAS [8-13] etc. have been used. Many of these are time consuming or require complicated and expensive instruments. Thus a method which could detect copper rapidly and conveniently has been searched.

2. Experimental

2.2.1 Apparatus and software: JEOL JSM -6390 SEM, The scanner (HP-SCANJET G2410), the MATLAB software, MICROLITE micro pipette were used.

2.2.2 Chemicals and Reagents: All reagents used were analytical grade chemicals. Double distilled water is used throughout the experiment. A stock of 5000 µg mL-1 and 1% solution of oxalic acid and resorcinol (1:1 by weight) were used.

2.2.3 Procedure: In presence of copper a deep magenta red colored spot is produced on the paptode. To construct the paptode strips of Whatman filter paper were immersed in 1% solution of 1:1 solution of oxalic acid and resorcinol for few seconds and then dried in a temperature controlled oven (to speed up drying). Aliquots of 12µL of copper solutions were injected on these strips and then strips are heated at 60-700C in an oven for 15 minute to develop the spot. The strips were scanned and R, G and B values of spots were recorded by MATLAB after development of spot. Any color can be analyzed to obtain its corresponding R, G and B value. Effective intensity for any color values of color spots was calculated by following formulae:

Ar = -Log (Rs/Rb) ---------- (1); Ag = -Log (Gs/Gb) ---------- (2); Ab = -Log (Bs/Bb) ---------- (3)

Where, Ar, Ag, Ab are effective intensities of red, green and blue color respectively ,Rs, Gs, Bs and Rb, Gb, Bb refer to R, G and B values of sample and blank respectively.

3. Results and Discussions: Optimization of conditions:

3.3.1 Injection volume: The optimum sample volume was obtained to be 12µL.Increased volume injection leads to more diffusion of spots and thus consequently decreases the intensity of color.

3.3.2 Effect of oxalic acid and resorcinol (1:1 by weight) mixture: In order to study the effect of reagent, solutions with various concentrations of reagent was prepared and immobilized on Whatman paper strips and then allowed to dry. After drying optimized volume of a standard solution containing 1000µg mL^{-1} of copper was injected on each strip and analyzed as reported. The effective intensities of R, G and B values were plotted vs. concentration of reagent mixture. At 1% concentration of reagent mixture maximum color intensity was observed and hence selected as optimum.

3.3.3 Effect of Temperature: The effect of temperature has been studied from room temperature to 100^0C after injection of copper. The maximum colored intensity was found between temperatures 80-90^0C and hence selected as optimum for analysis.

3.3.4 Drying Methods: Different methods of drying such as drying at room temperature, oven and hot air were used for drying the strips after injection of reagent onto strips but no considerable change in signals was observed. However, an oven is recommended for increasing the rate of drying.

3.3.5 Response Time; Stability of spots; Stability of sensor and Detection Limit (DL): The response time of the system was evaluated under optimum conditions for 1000µg mL^{-1}. In the proposed method spot of maximum color intensity develops after 15 minute. Scanning of the sensor was done in the time period of 15, 30, 60,120, 180 and 240 minute and then after 24hr and 48 hr. The developed spot remain stable for more than two days. No significant change was observed within 40 days, when the paptode is used periodically each day after its preparation. Therefore, the prepared sensor can be used at best for 40 days. For each RGB factor there is one DL [1].Theoretical DL_s of the method were 0.24 µg mL^{-1} for R, B and G values. Practical DL determined was 15 ng mL^{-1}. The practical DL is the lowest concentration, which gives color on strip.

3.3.6 Calibration Curves: For obtaining calibration curve the effective intensities of spot were plotted against 100-1000 µg mL^{-1} of copper for all three values (R, G and B).The increase in effective intensity with increasing concentration has been observed till 700 µg mL^{-1} for G and B values ; R values are inconsistent hence not considered (figure 1). B values are higher but G values have higher linearity co-efficient (R^2=0.9912). Therefore, G values are recommended for their high sensitivity and reproducibility (figure 2).

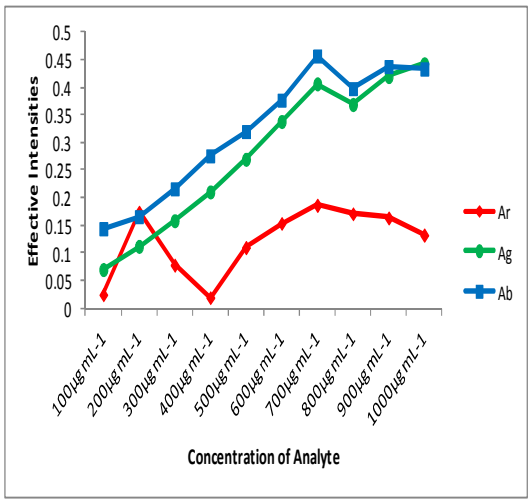

Figure: 1 Calibration 1-1000µg mL^{-1}

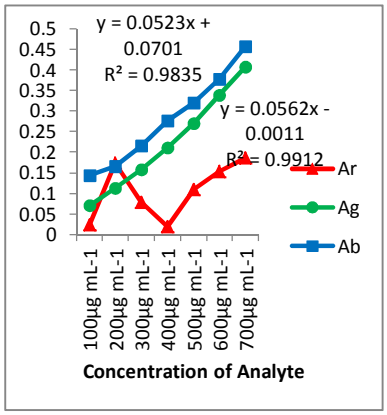

Figure: 2 Calibration 1-700µg mL^{-1}

Interferences: Interference of various species including pesticides have been checked for100µg mL^{-1} of $CuSO_4$ and following limits have been obtained.

Ammonia (120), Phenol and Salphamic acid (500),Benzene(1000), Nitrate (300), Ascorbic acid (4000), Semi carbazides (1500), FAS and Dimethyl sulphate (7000), Nitrobenzene (800), Pyridine (700), Salicaldehyde (200), Hydrazine(300), Endosulfan and Thiram (2000), diphenylamine (150), nitrobenzene (700), 5-sulphosalicilic acid (600), Cl^-,SO_4^{2-},CO_3^{2-},Na^+,K^+ Ca^{2+}(7000), Cd^{2+}, Zn^{2+}, $Ba^{2+}$$Hg^{2+}$ (5000), Pb^{2+}(500), As^{3+}, Se^{4+}(1000), Fe^{3+} ,Al^{3+}, Mg^{2+}(10000)

Application of Disposable paptode: The prepared paptodes were successfully applied to determine Cu in different samples containing known amount of $CuSO_4$ which is equivalent to Cu (II).

Conclusion: The proposed method is found to be superior and produces quantitative results for determination of copper. The method described in present paper has many advantages: it does not need any expensive instrument,

it is simple and rapid. The available commercial testing strips are semi quantitative while the developed paptodes are quantitative as well as best of our knowledge no such strips are available for it. Thus the chemo sensor can be used in for testing copper.

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