

## Cadmium Ion Sensing Paptode Based On Digital RGB Color Analysis

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**Abstract:** A new optical analytical method, “**digital RGB Analysis**” is proposed based on MATLAB image processing tool 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. Image processing tool can simulate the optimum color variations by optimization of visual color sensor with computer assistance and thus make colorimetry (semi quantitative analysis) as an accurate determination method. The optode was constructed by immobilizing ninhydrin on TLC (thin layer chromatographic) paper. The reaction is based on complexation of ninhydrin with cadmium to result into a light purple to magenta colored spot followed by scanner based detection. Changes in **RGB** values of color spots on TLCstrips create a pattern. The obtained pattern was analyzed using image processing tool of **MATLAB** software to determine cadmium. All parameters affecting intensity on optode have been optimized. The proposed sensor was linear in the range 0.018-0.54 $\mu\text{g mL}^{-1}$  ( $R^2=0.996$ ) for G values and can sense up to 3ng  $\text{mL}^{-1}$ . SEM investigation of dye has also been done. The proportionality in intensity of the spot color on the optodes loaded with varying amounts of cadmium suggests its potential applications for determination of it in various samples. The **paper optode** can be used for pollutant check and even health check at home. Thus the paper optode has great potential for this purpose.

**Keywords:** MATLAB, nano dye particle paptode, RGB, thin layer chromatographic paper .

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### I. Introduction

Cadmium is one of the heavy metals more critical for the human health<sup>[1]</sup>. It enters the organism primarily via the alimentary and/or respiratory tract. It can be cause of diseases as: hypertension, arteriosclerosis, cancer, etc. Considering it, health organizations have established permissible limits for cadmium in food, including drinking water. The World Health Organization (WHO) established as 3 $\mu\text{gL}^{-1}$  the maximum permissible for this element in drinking water. The limit established by Environmental Protection Agency (EPA) is 5 $\mu\text{gL}^{-1}$ <sup>[2,3]</sup>.

The most human cadmium exposure comes from the tobacco smoke and from ingestion of food which most of that arises from the uptake of cadmium by plants from fertilizers, sewage sludge, manure and atmospheric deposition<sup>[1,4]</sup>. More recently, the possible role of cadmium in human carcinogenesis has been also studied<sup>[4,5]</sup>.

Nowadays, cadmium is of interest as a toxic environmental pollutant since it has many adverse effects on humans, plants and animals. The need to monitor cadmium contamination in the environment at ever decreasing concentrations provides a driving force for the development of methods that are accurate and have low limits of detection, but are also simple, rapid, and inexpensive. Spot test analysis has been extensively studied for qualitative determination of materials on an absorbent material<sup>[6]</sup>. Reflectance spectroscopy cannot yield precision better than 10% when used to obtain quantitative data directly from spot test analysis<sup>[7]</sup>. Therefore, the results obtained from spot test analysis were considered unreliable but use of MATLAB software in the present method resulted into quantitative and reproducible spot test analysis.

Test strips for semi quantitative determination has been reported by Amlathe et al<sup>[8]</sup>. DCA Analysis for lithium has also been reported<sup>[9]</sup>. Paptodes for quantitative determination of various metal ions As, Fe, Hg, Zn and Se have been reported<sup>[10-16]</sup>. The paptode is simply a paper or other ordinary porous material such as clay or cotton or Whatman filter paper or ordinary filter paper or even TLC can be used as a substrate support for reagent. A thorough description of RGB analysis has been described by Amlathe and co-workers<sup>[10]</sup>.

The usual methods for determination of cadmium involve Electrothermal atomization, GFAAS, Electrothermal Atomic Absorption spectrometry, Extraction spectrophotometry, Kinetic spectrophotometry, pulse polarography, spectrophotometry, Zeeman background correction, ICPMS, radiochemical neutron activation analysis etc.<sup>[17-26]</sup>. These methods are not compatible in terms of simplicity and economy. **Colorimetry is the most appropriate choice due to its visible signal transduction in the presence of target. Besides, the reagents for colorimetry are most probable to be commercialized represented as pH paper, mercoquant, EMquant, ELISA, Quantafix etc.**

In the proposed method, we have described the use of paptode for analysis of cadmium. In the proposed sensor 1% ninhydrin solution was immobilized on TLC strips followed by drying. After injection of cadmium sample, a light purple to magenta colored spot of product (ninhydrin cadmium complex) was formed on the paptode. Blank also produces a light blue coloration in similar conditions that apparently seems similar to the color produced by lower concentration of cadmium but RGB values are much different. After drying of the spot, an image of each strip was recorded using a scanner. The color values of the spots were analyzed with MATLAB.

## II. Experimental

2.1 Apparatus and software: JEOL JSM -6390 A SEM Made in Japan, JEOL JFC-1600 Sputter Coater unit.

The scanner (HP-SCANJET G2410). Resolution of scanner was regulated at 300 dpi. For analyzing color values in RGB (red, green, blue) system, the MATLAB software, which was written in Visual Basic 6 Media, was used.

A MICROLITE micro pipette was used for injecting samples on strips.

2.2 Chemicals and Reagents: All reagents used were analytical grade chemicals. Double distilled water is used throughout the experiment.

Cadmium stock-A stock of 1000  $\mu\text{g mL}^{-1}$  was prepared by dissolving 163.07 mg of  $\text{CdCl}_2$  in 100 ml of double distilled water.

Ninhydrin -1% ninhydrin solution was prepared by dissolving 1g ninhydrin in acetone and then making up to 100ml by double distilled water.

## III. Procedure

In presence of cadmium a light purple to magenta colored (depending upon the concentration) spot is produced on the sensors. To construct the sensor strips for cadmium, strips of TLC paper were immersed in 1% solution of ninhydrin for few seconds and then dried in a temperature controlled oven (to speed up drying). Aliquots of 18  $\mu\text{L}$  of cadmium solutions were injected on these strips and then strips are heated at 60-70 $^{\circ}\text{C}$  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. The RGB color model is an additive color model in which red, green and blue light are added in various ways to produce a broad array of colors. 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:

$$A_r = -\text{Log} (R_s/R_b) \quad (1)$$

$$A_g = -\text{Log} (G_s/G_b) \quad (2)$$

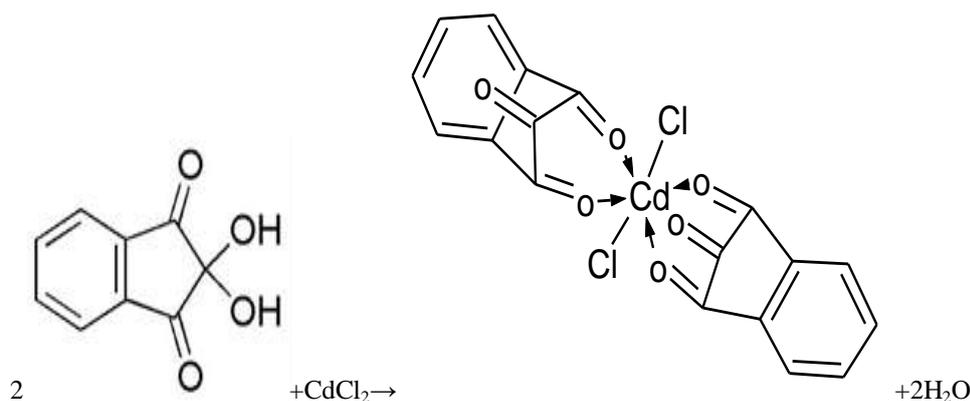
$$A_b = -\text{Log} (B_s/B_b) \quad (3)$$

Where,  $A_r, A_g, A_b$  are effective intensities of red, green and blue color respectively,  $R_s, G_s, B_s$  and  $R_b, G_b, B_b$  refer to R, G and B values of sample and blank respectively. The calibration curve is obtained by plotting effective intensities of R, G and B values vs. analyte concentration.

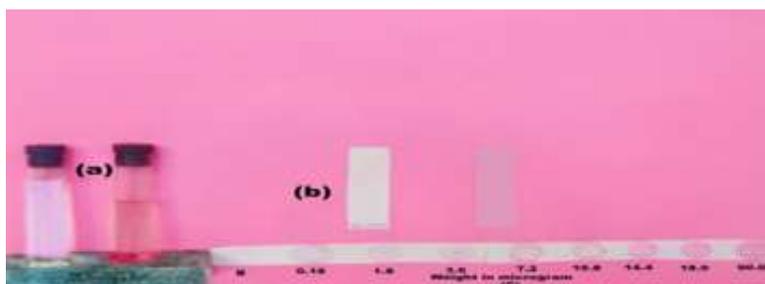
## IV. Results And Discussion

### 4.1 Chemical Reaction

Ninhydrin forms a complex structure with cadmium to give the probable structure analogous to divalent metal complex with Schiff's base [27] when two ninhydrin molecules get co-ordinated with cadmium. Absence of acid formation is co-checked by phenolphthalein and methyl orange.



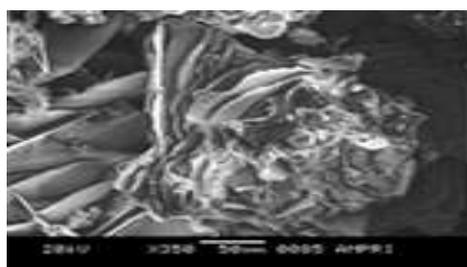
**PHOTOGRAPH SHOWING COLOR VARIATION BEFORE AND AFTER ADDING CADMIUM SAMPLE**



Where; (a) – Color development in solution; (b) – Color development on strip and (c)– Color variation on strip for different concentrations of cadmium

**4.2 SEM Investigation**

The dye has also been examined using scanning electron microscope (SEM) after gold coating. In SEM images dye appears a flower like structure with needles and petals. The size of petals and diameter of needles may be expected in nano meter as the images reveal.

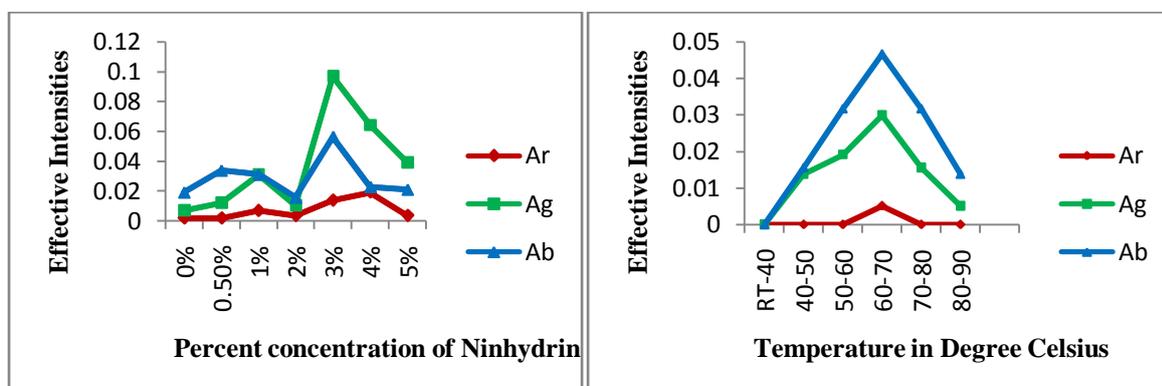


**MICROGRAPH**

**4.3 Optimization of conditions:**

**Injection volume:**The influence of volume of analyte which must be injected onto strip was investigated. The optimum sample volume was obtained to be 18µL. Increased volume injection leads to more diffusion of spots and thus consequently decreases the intensity of color.

**Effect of reagent concentration:**In order to study the effect of ninhydrin concentration, solutions with various concentrations of reagent was prepared and immobilized on TLC paper strips and then allowed to dry. After drying 18µL of a standard solution containing 40µg mL<sup>-1</sup> of cadmium was injected on each strip. After heating for 15 minute at 60-70°C, the strips were scanned and their colors were analyzed by the software, and the effective intensities of R, G and B values were plotted vs. concentration of ninhydrin. Figure 1 show the effect of ninhydrin concentration on spot intensities. At 1% concentration of ninhydrin maximum color intensity was observed and hence selected as optimum (figure 1).



**Fig.: 1 Effect of ninhydrin concentration Fig.: 2: Effect of Temperature**

**4.3.1 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.

4.3.2 Effect of Temperature: The effect of temperature has been studied from room temperature to 90°C after injection of 40 µg mL<sup>-1</sup> of cadmium. It has been found that the development of colored spot does not take place below 40°C. The intensity was found to be increased from 40-70°C and then observed to be decreased. The maximum colored intensity was found between temperatures 60-70°C and hence selected as optimum for analysis (figure 2).

4.3.3 Response Time: The response time of the system was evaluated under optimum conditions for 40 µg mL<sup>-1</sup>. It is the time required to achieve maximum color intensity. In the proposed method spot of maximum color intensity develops after 15 minute.

4.3.4 Stability of spots: To study the stability of color spots, 40 µg mL<sup>-1</sup> of cadmium was injected under optimum conditions on the sensor. 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.

4.3.5 Stability of sensor: To study the stability of sensor, after immobilizing reagent on the Whatman paper strip, it was used periodically each day. No significant change was observed within 20 days, afterwards spot lesser intensity develops. After 30<sup>th</sup> day spot of a very poor intensity develops with a response time of more than 30 minute. Therefore, the prepared sensor can be used at best for 20 days and on a stretch for one month. The sensors were stored in dark to avoid any possibility of environmental oxidation of ninhydrin.

4.3.6 Detection Limit (DL): **The practical DL is the lowest concentration, which gives color on strip no matter falls in linearity range or not.** For each RGB factor there is one DL<sup>[11]</sup>. Theoretical DL<sub>s</sub> of the method were 0.18 µg mL<sup>-1</sup> for R, B and 0.018 for G values respectively. All three values can be considered but G values are more sensitive and follow the standard linearity pattern as shown in figure 3 by trend line therefore, values are recommended for determination. Practical DL determined was 3ng mL<sup>-1</sup>.

4.3.7 Calibration Curves: For obtaining calibration curve the effective intensities of spot were plotted against 1-100 µg mL<sup>-1</sup> of cadmium for all three values (R, G and B). The increase in effective intensity with increasing concentration has been observed but the standard linearity pattern has been found in between the different concentrations. **Change in linearity pattern occur due to change in shade of color and hence RGB pattern.** In figure S1 (Supplementary information) calibration curves for 0.5-40 µg mL<sup>-1</sup> of cadmium has been shown. From figure S2 (Supplementary information), it is clear that rather G values are higher but linearity co-efficient (R<sup>2</sup>=0.99) is higher for R values. Figure 3 show the higher G values as well as higher linearity co-efficient (R<sup>2</sup>=0.996). Therefore, both R and G values can be equally considered but G values are recommended for their high sensitivity and reproducibility.

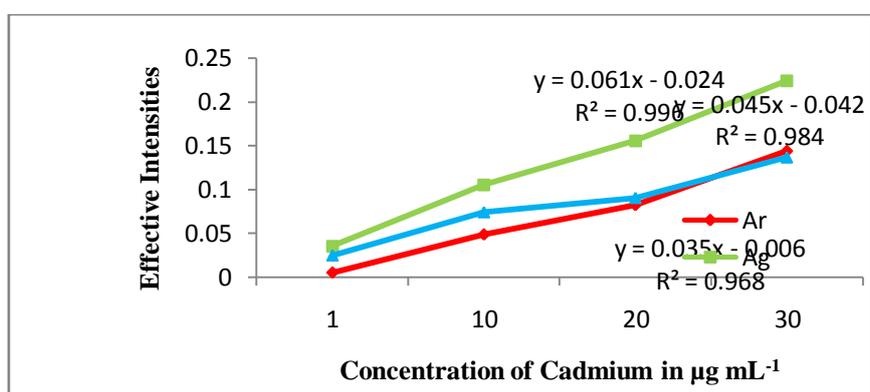


Fig.: 3 Calibration curve for 1-30 µg mL<sup>-1</sup>

Reproducibility of the system: Reproducibility of sensor has been investigated at seven different sensors under optimum conditions for various concentrations of cadmium. The results are reported in table 1 and conclude that the proposed method is reproducible.

**Table: 1 Average, SD (standard deviation) and RSD (relative standard deviation) of seven repetitive analyses**

S. No.	$\mu\text{g mL}^{-1}$ of cadmium solution	$A_r$			$A_g$			$A_b$		
		Avg.	SD	RSD%	Avg.	SD	RSD%	Avg.	SD	RSD%
1.	1	0.0053	0.003	56.6	0.035	0.0012	2.85	0.0253	0.0016	6.65
2.	20	0.0837	0.0035	4.17	0.1553	0.0015	1.01	0.0897	0.0021	2.40
3.	40	0.1767	0.0051	2.88	0.2395	0.003	1.25	0.1581	0.0035	2.21

4.3.8 Interference studies: To study the selectivity of the proposed method, the effect of various species on the determination of  $40\mu\text{g mL}^{-1}$  of cadmium was tested under optimum conditions without any masking. The tolerance limit was defined as the concentration of the added species that causes  $\pm 5\%$  relative error. Results reveal that except  $\text{Al}^{3+}$  there is no interference offered by other metal ions (Table 2).

**Table: 2: Tolerance limit of various interfering species on determination of cadmium**

S.No.	Interfering species	Tolerance limit ( $\text{mgL}^{-1}$ )
1	$\text{Mn}^{2+}, \text{Na}^+, \text{HCO}_3^{2-}$	200
2	$\text{K}^+, \text{Cr}^{3+}, \text{NH}_3$	1000
3	$\text{As}^{3+}$	400
4	$\text{Se}^{3+}$	250
5	$\text{Fe}^{2+}, \text{NH}_4^+, \text{SO}_4^{2-}, \text{Ba}^{2+}, \text{Cl}^-, \text{Zn}^{2+}$	5000
6	$\text{Cu}^{2+}, \text{Ca}^{2+}$	250
7	$\text{Al}^{3+}$	80
8	$\text{Hg}^{2+}, \text{Pb}^+$	500

## V. Application Of Disposable Sensors

### 5.1 In Analysis of real samples:

The proposed sensor has been successfully applied for determination of cadmium in various samples by developed as well as reported method [25]. Using the calibration curve, the concentration of cadmium in rice, wheat, tap water, effluent water and urine samples were calculated. The results are given in Table 3. The results reveal that cadmium can be determined quantitatively in the region assessed.

**Table: 3: Percent recovery of cadmium in environmental samples.**

S. No.	Sample	Cadmium originally found	Cadmium added	Total cadmium found	% recovery by developed method	% recovery by reported method
1	Effluent Water	1	10 $\mu\text{g}$	10 $\mu\text{g}$	90.9	90.6
		2	0.8 $\mu\text{g}$	20 $\mu\text{g}$	96.1	95.2
		3	0.6 $\mu\text{g}$	30 $\mu\text{g}$	99.6	98.6
2	Tap Water	1	10 $\mu\text{g}$	10.0 $\mu\text{g}$	100.0	99.9
		2	20 $\mu\text{g}$	19.5 $\mu\text{g}$	97.5	96.4
		3	30 $\mu\text{g}$	28.5 $\mu\text{g}$	95.0	94.0
3	Rice	1	10 $\mu\text{g}$	12.0 $\mu\text{g}$	100.0	98.4
		2	20 $\mu\text{g}$	20.5 $\mu\text{g}$	97.6	95.2
		3	30 $\mu\text{g}$	32.0 $\mu\text{g}$	100.0	98.7
4	Wheat	1	10 $\mu\text{g}$	13.0 $\mu\text{g}$	92.8	91.0
		2	20 $\mu\text{g}$	23.0 $\mu\text{g}$	92.0	91.2
		3	30 $\mu\text{g}$	31.0 $\mu\text{g}$	91.1	90.8
5	Urine	1	10 $\mu\text{g}$	11.0 $\mu\text{g}$	~ 100.4	100.0
		2	20 $\mu\text{g}$	20.5 $\mu\text{g}$	~ 100.0	99.6
		3	30 $\mu\text{g}$	30.0 $\mu\text{g}$	~ 98.3	99.3

### 5.2 In Removal of Cadmium: As Filter

Cadmium poses a series risk to the environment and endangers public health. Presence of it in drinking water system is a potential health hazard. Therefore, they should be removed from water and wastewaters before discharge. Thus, there is a hunger need for a cost effective method for removal of cadmium from water. There are many methods available in literature for removal of heavy metals from aqueous samples [28-39]. However;

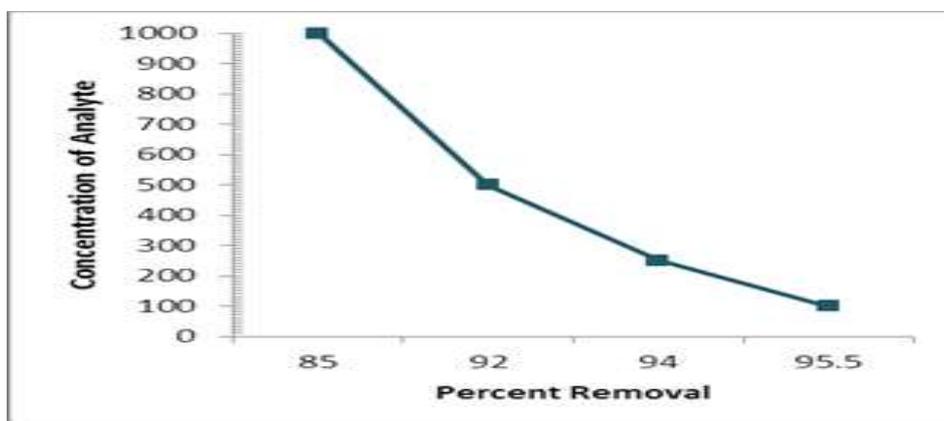
complete elimination of heavy metals at very low concentrations through these is not possible; are expensive as these require advanced equipment and high energy.

The paptode based on RGB analysis was successfully applied for removal of cadmium from aqueous sample. Cadmium may be discharged to water through fertilizers, manure and sewage [1, 4]. Real samples containing Cd were not available hence synthetic samples were prepared by adding a known amount of Cadmium to water.

The constructed paptode is used as filter for removal of cadmium. Cadmium sample containing different concentration are allowed to be filtered through it in batches and the sensors were scanned before and after adsorption to know the change in RGB values. It is observed that with lower concentrations adsorption was more i.e. sensors become more effective (Figure: 5). Results of percent adsorption are reported in Table: 4. The disposable filter is allowed to remain in contact of  $40\mu\text{g mL}^{-1}$  cadmium solution for an hour and change in B value is observed at every 15 minute. It is found that best adsorption took place within 15 minute.

S. No.	Concentration of cadmium before removal ( $\mu\text{g mL}^{-1}$ )	Concentration of cadmium after removal ( $\mu\text{g mL}^{-1}$ )	Percent removal
1	1000	150	85.0
2	500	40	92.0
3	250	15	94.0
4	100	0.5	95.5

**Table: 4: Percent Removal of cadmium**



**Fig.: 5: Percent Removal of Analyte**

## VI. Conclusions

The proposed method is found to be superior and produces quantitative results for determination over existing methods. The method described is advantageous being non instrumental, simple and rapid, wider linear range, application do not require any skilled labor or operation (Table 5). The method is also applicable for effective removal of cadmium. The shorter response time, portability, ease of reagent immobilization, instantaneity to adsorb and remove cadmium are considerable advantages of developed paptode. The paptode has been successfully used for testing and removing cadmium on the spot in various food and biological samples.

**Table: 5 Comparison of proposed method with other methods**

S. No.	Reagents	Method	Range of Determination	Detection Limit	Remarks
1	TritonX-100, $\text{HNO}_3$ <sup>[17]</sup>	Electrothermal Atomization	0.05-3.0ng $\text{mL}^{-1}$	NA	High Skilled operation is required, expensive, Very low volume is required.
2	Di thiozone, Naphthalene <sup>[18]</sup>	GFAAS	-	1.2ng $\text{L}^{-1}$	Complicated, expensive
3	Arsenazo I, Hydrogen	Kinetic	0.002-0.25 $\mu\text{g}$	NA	Non

	peroxide <sup>[21]</sup>	spectrophotometry	mL <sup>-1</sup>		selective, Mg <sup>2+</sup> , Ca <sup>2+</sup> , Zn <sup>2+</sup> and Sn <sup>2+</sup> interfere
4	1-(2-pyridilazo)-2-naphthol <sup>[22]</sup>	Pulse polarography	0.1-150 µg mL <sup>-1</sup>	70.0 ng mL <sup>-1</sup>	Less sensitive, Time consuming
5	2-Hydroxy- 4-n-butoxy-5-bromopropiophenone thiosemicarbazone <sup>[23]</sup>	Spectrophotometry	15.62-16.86 µg mL <sup>-1</sup>	NA	Less sensitive, a traditional method
6	0-Carboxybenzenediazoaminobenzene-p-azo Benzene <sup>[24]</sup>	Spectrophotometry	0.1-0.9 µg mL <sup>-1</sup>	NA	pH dependent
7	Ninhydrin (present method)	MATLAB assisted RGB analysis	0.018-0.54 µg mL <sup>-1</sup>	3 ng mL <sup>-1</sup>	Highly sensitive, Quantitative, Rapid, removal is possible

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