



An analytical study by Spectrophotometric method for determination of cobalt (II) in aqueous solutions by using organic reagent (HPHMAB)

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Abstract The study examined the possibility of forming a colored complex between cobalt (II) and 4-hydroxy-3]] (2-hydroxyphenyl) Methane [amino benzene sulfonic acid (HPHMAB) to be used in determination of cobalt (II) in aqueous solutions.

It was found that the reagent is formed with cobalt (II) yellow orange complex at pH = 10. The Absorbance of the complex was measured at 430 nm and that wavelength is used to determine all the quantitative evidence related to this complex, so The stoichiometric composition for formation complex between HPHMAB and cobalt (II) (1: 4), and the value of molar absorption factor was $\epsilon = 1.4762 \times 10^4 \text{ l.mol}^{-1}.\text{cm}^{-1}$ and constant formed the complex $K_{\beta} = 2.746 \times 10^3$. The Linearity was in the range (0.1-4) mg / l and with a detection limit 0.05 mg / l, the relative standard deviation did not exceed 2.85% in the worst case and the recovery was not less than 93% when applying this method to standard samples of cobalt, which confirms the possibility of using the HPHMAB detector to determine cobalt (II).

Keywords HPHMAB, Spectrophotometric method, cobalt (II), molar absorption, maximum absorbance

1. Introduction

Cobalt is an important transition element in industry, due to its many uses in the manufacture of alloys, pigments, catalysts and galvanic coatings [1]. Long term exposure to high levels of cobalt leads to reduced fertility in men, vomiting, nausea, pulmonary and skin diseases. Intake high dose of cobalt may lead to damage heart muscle and thyroid gland and increase in red blood cell production, while low levels lead to anemia and red blood cell disease, in addition to fatal disorders and low levels are necessary for the work of enzymes in mammals; cobalt is a major component of vitamin B12, but it is very toxic when it is in high levels for plants.

Various techniques and analytical methods have been used to determine cobalt levels in different samples such as atomic absorption, chromatography, XRF, but spectroscopic methods using organic reagents are the most used methods due to their speed, low cost, simpler procedures, and wide application. Where all studies recommended the search for new organic reagents with different functional groups.

A quick and sensitive spectral determination method for the determination of cobalt (II) was developed using a 5-bromo-2-hydroxy-3-methoxy benzaldehyde-4 hydroxybenzoyehydrazone, Which formed a complex brown color when $\lambda_{\text{max}} = 416 \text{ nm}$ In the field of acidity ranging from [6-8], The value of both molar absorption coefficient and Sandal sensitivity was $2.0246 \times 10^4 \text{ l.mol}^{-1}.\text{cm}^{-1}$ and $0.0029 \text{ mg} / \text{cm}^2$ respectively, The Pierre-Lambert law was achieved in the range (0.177-2.94) mg / ml, with a detection limit of $0.016 \mu\text{g} / \text{ml}$ [5]. The ditizone detector was



also used to determine cobalt (II) in alkaline environment (pH = 9) at $\lambda_{\max} = 570$ nm. The detection limit and the quantification limit were 1.46×10^{-2} mg / l and 4.87×10^{-2} mg / l Respectively, Linearity was achieved in the range of concentrations (0.3-6) mg / l [6]. cobalt(II) was selected using the detector (3 - 2 - theozolel) - 2,6 - diamino pyridine, which formed a green complex at $\lambda_{\max} = 598$ nm, pH = 10, linearity in the concentration range (2×10^{-6} - 1.2×10^{-5})mol / l, the detection limit and the molar absorption coefficient were 5.26×10^{-7} mol / l and 1.52×10^4 l.mol⁻¹.cm⁻¹, respectively [7]. A spectral spectroscopy method was developed to determine cobalt (II) using the 2-carboxyldehyde thiosymecarbazone reagent, which was a yellow complex, which in turn was extracted by isobutanolat pH= 6 and the complex was stable for more than 24 hours. Linearity ranged in concentrations (0.236-2.36) μ g / ml, The value of both molar absorption coefficient was 1.86×10^4 l.mol⁻¹.cm⁻¹ and detection limit 0.0028 μ g / ml. [8].

Materials and Apparatus

Spectroscopy of visible rays Ultraviolet and dual-pack produced by OPTIMA model SP-3000, 2-amino-phenol-4-sulfonic acid, acetone, methanol, ethanol, Acetone, Methanol, ethanol, salicyl aldehyde acid, acetaldehyde, boron acid, Hydrochloric acid, Sulfuric acid, acetic acid, Phosphoric acid, cobalt chloride.

Results and Discussion

1. Studying of complex formation between cobalt (II) and HPHMAB reagent

It was Noticed the beginning of discoloration of cobalt (II) -containing solutions in orange-yellow color Within a range of pH levels ranging from 5-12 with a britton buffer, While the blank solutions were pale yellow, and when the spectral survey of the visible and ultraviolet field showed a peak absorption at 430 nm. This shows the complex formation between cobalt (II) and the proposed reagent, Where the Complex uptake was increased with pH increasing for britton buffer to reach its λ_{\max} value at pH = 10 to return and decrease after that value, repeating the previous experiment again but having the acetate buffer once again and the phosphate buffer again, the optimum pH value was 9 for the acetate buffer and pH = 7 for phosphate buffer, Figure (1).

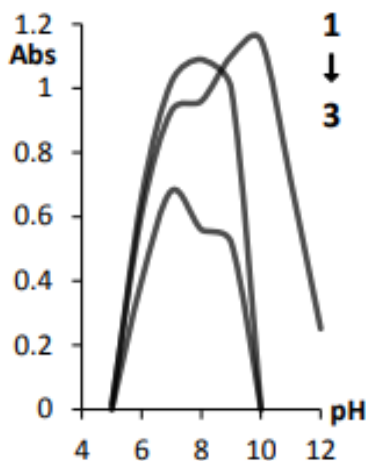


Figure 1: Change the absorption of the complex HPHMAB- Co^{2+} by changing the pH values of the solution for different buffers.

$$[\text{HPHMAB}] = 6.7852 \times 10^{-4} \text{ M}, [\text{Co}^{2+}] = 6.7852 \times 10^{-5} \text{ M}.$$

1- Britton buffer, 2- acetate buffer, 3-phosphate buffer, $\lambda_{\max} = 430$ nm.

2. Choosing the best buffer solution

In this study, the complexity of the complex was determined at the optimum pH for each buffer, is pH = 10 for britton buffer, pH = 9 for the acetate buffer and pH = 7 for the phosphate buffer, one of the flasks was left without adding a buffer to the comparison.



When the spectral survey was conducted, it was noticed the complex absorption remained almost constant in the existence of the three buffers, while it was low in the absence of buffer. In observing the complex absorption of the complex over time, it was found that the absorption of the complex remained constant for 24 hours with the three buffers. So the addition of the britton buffer was adopted in subsequent studies.

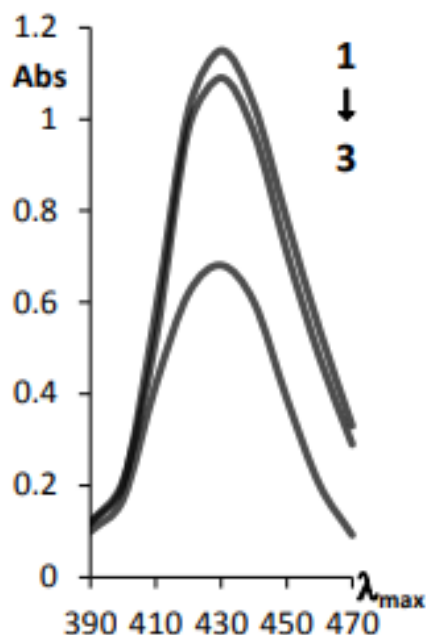


Figure 2: Spectroscopy of the complex HPHMAB- Co^{2+} using three buffer solutions as follows: 1 (britton), 2 (acetate), 3 (phosphate). $\lambda_{\text{max}} = 430 \text{ nm}$, $[\text{HPHMAB}] = 6.7852 \times 10^{-4} \text{ M}$, $[\text{Co}^{2+}] = 6.7852 \times 10^{-5} \text{ M}$

3. Choosing the best solution volume of britton bufferto form complex

The complex was formed by adding different volumes of the britton buffer at $\text{pH} = 10$ and 1 mL of the HPHMAB reagent in 25 mL volume flasks.

Figure 3 shows that the absorption of the complex increases at the beginning to reach the highest value when adding 1 mL of the buffer. It decreases and stabilizes approximately after 3 ml. Therefore, 1 mL of the britton buffer is added in subsequent studies, which is 4% of the volume of the beaker.

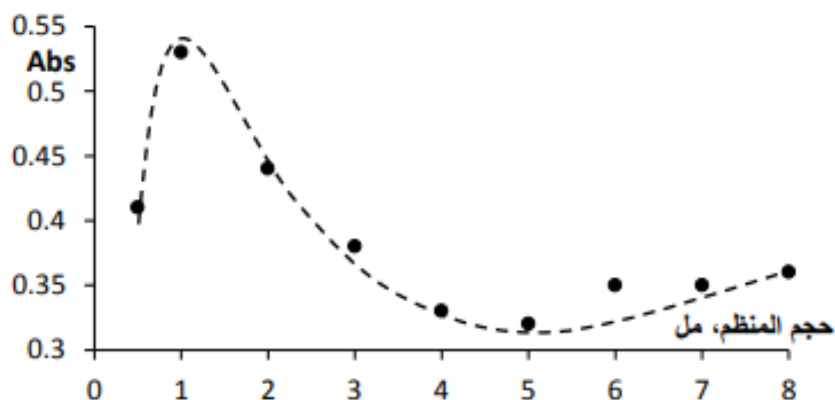


Figure 3: The relationship between the absorption of the complex and the volume of the britton buffer. $\text{pH} = 10$, $\lambda_{\text{max}} = 430 \text{ nm}$, $[\text{HPHMAM}] = 3.39384 \times 10^{-4} \text{ M}$, $[\text{Co}^{2+}] = 3.39384 \times 10^{-5} \text{ M}$



4. The Effect of temperature on the absorption of complex

The effect of temperature change on the absorption of the complex was studied within the range (25-90) °C spectral survey showed that at $\lambda_{\max}=430$ nm, the absorption of the complex increases with increasing temperature to reach the highest value at 50 °C.

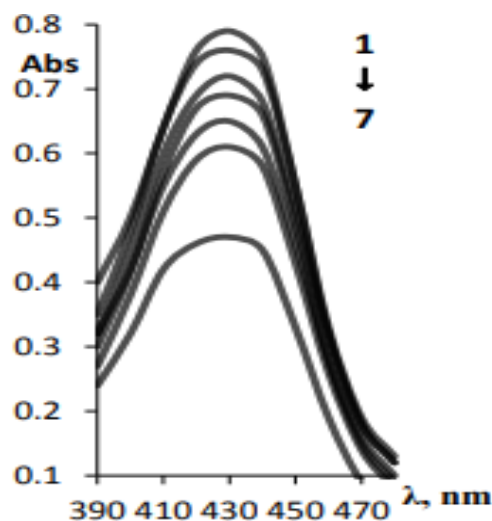


Figure 4: Complex spectroscopy Depending on the temperature.
 $pH=10$, $\lambda_{\max}=430$ nm, $[HPHMAM]=3.39384 \times 10^{-4} M$, $[Co^{2+}]=3.39384 \times 10^{-5} M$
1(50), 2(60), 3(70), 4(40), 5(90), 6(80), 7(25).

5. Effect of heating time on complex absorption

The relationship between absorption and heating time was studied. It was found that the absorption of the complex decreases with increasing heating time, so the optimal heating time was 5 min (Fig. 5).

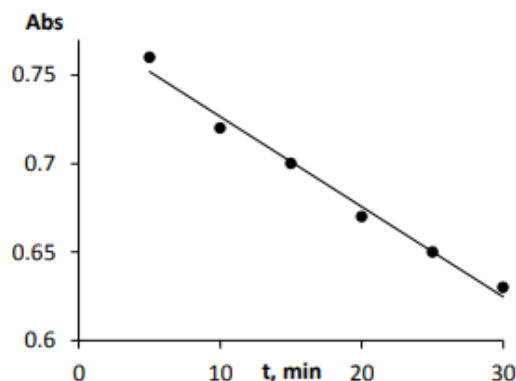


Figure 5: The relationship between the absorption of the complex and heating time.
 $pH=10$, $\lambda_{\max}=430$ nm, $[HPHMAM]=3.39384 \times 10^{-4} M$, $[Co^{2+}]=3.39384 \times 10^{-5} M$

6. Effect of some hydrophilic organic solvents in the absorption of complex

The effect of organic solvents was estimated at seven percentage, ranging between (2-40)%. After the spectroscopy, it was determined that the complex was formed regardless of the nature of the added solvent and its percentage in Table (1), and that the absorption values were close in case of solvent or non-existent with a slight decrease when using methanol and ethanol. Therefore, the formation of the complex was adopted in a sterile water medium without the addition of any organic solvent to the medium of reaction in subsequent studies.

Table 1: Change the absorption of the complex HPHMAB-Co²⁺ with the changed nature and percentage of the added organic solvent.pH= 10, λ_{\max} =430 nm, [HPHMAB]= 3.39384×10⁻⁴M, [Co²⁺]= 3.39384×10⁻⁵M, T= 50°C, t=5min

PropaneDiol 2,1	Ethyl glycol	AcetAldehyd	Ethanol	Methanol	Acetonitrile	Acetone	Solvent type
0.72	0.71	0.74	0.66	0.65	0.75	0.74	2
0.71	0.72	0.73	0.65	0.66	0.75	0.76	4
0.72	0.73	0.73	0.64	0.64	0.74	0.75	8
0.73	0.71	0.71	0.65	0.63	0.75	0.71	16
0.71	0.70	0.71	0.62	0.62	0.73	0.7	24
0.70	0.70	0.70	0.61	0.61	0.71	0.71	32
0.70	0.70	0.70	0.62	0.61	0.71	0.72	40

Complex absorption without adding solvent = 0.77

7. Sequence of additions to Complex Formation Co (HPHMAB)

After examining the conditions prior to the formation of complex HPHMAB-Co²⁺, the sequence of additives used in different ways was changed as follows:

- Cobalt (II), Reagent, britton./- Cobalt (II), britton, Reagent. / - Reagent, Cobalt (II), britton.

- Reagent, britton, Cobalt (II). -britton, Cobalt (II), Reagent. / -

After spectroscopy and absorbance measurements at λ_{\max} = 430 nm, it was found that the studied complex was formed no matter how different the additive method was and with similar absorptive and was the best when following the sequence:

Reagent, britton, cobalt (II), heating, leaves the solution in the laboratory atmosphere and then completes the volume with double distillation water until the capacitance marker, which is adopted in subsequent studies.

8. The effect of increasing the concentration of the reagent in the absorption of the complex

The effect of increasing the concentration of the reagent on the absorption of the complex HPHMAB-Co²⁺ was studied for different concentrations of cobalt (II) 0.84846 × 10⁻⁵M and 3.39384 × 10⁻⁵ M and different concentrations of the detector ranged from (0.084846-4.24231) × 10⁻⁴ M for the first concentration of cobalt (II) and (0.33939-30.54474) × 10⁻⁴ M separately. After the measurement of the absorption of solutions prepared at λ_{\max} = 430 nm, it was shown to increase with the increase of the reagent concentration to its λ_{\max} value at the concentration of the reagent at 0.84846 × 10⁻⁴ M and 3.39386 × 10⁻⁴ M,). And then remain constant with continuous increase in the concentration of the reagent table (2).

Table 2: Change the absorption of the complex HPHMAB-Co²⁺ by changing the concentration of the HPHMAB reagent, pH= 10, λ_{\max} = 430 nm, T= 50°C, t=5min, Percentage of britton buffer 4%

$C_{\text{HPHMAB}} \times 10^{-4} \text{ M}$	Complex absorption [Co ²⁺]= 3.39384×10 ⁻⁵ M	$C_{\text{HPHMAB}} \times 10^{-4} \text{ M}$	Complex absorption [Co ²⁺]= 0.84846×10 ⁻⁵ M
0.33939	0.05	0.084846	0.01
0.67877	0.15	0.169692	0.025
1.35755	0.26	0.254539	0.042
2.03632	0.42	0.339385	0.06
2.71509	0.66	0.42423	0.09
3.39386	0.75	0.509077	0.15
6.78772	0.69	0.67877	0.1
10.18158	0.7	0.84846	0.21
13.57544	0.69	1.696924	0.21
16.9693	0.69	2.545386	0.2



20.36316	0.62	3.393848	0.18
23.75702	0.64	4.24231	0.17
27.15088	0.62	—	—
30.54474	0.64	—	—

Figure (6) The graphical relationship of the complex absorption change with the change of the detector concentration HPHMAB.

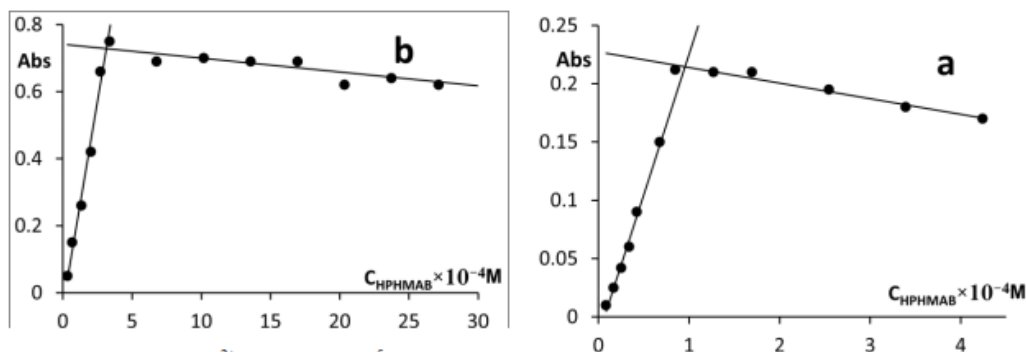


Figure (6): a - Absorption change with change of detector concentration at $[Co^{2+}] = 0.84846 \times 10^{-5} M$
 b- Absorption change with change of reagent concentration at $[Co^{2+}] = 3.39384 \times 10^{-5} M$
 $\lambda_{max} = 430 \text{ nm}$, $pH = 10$, $T = 50^{\circ}C$, $t = 5 \text{ min}$ • Percentage of buffer 4%.

9. Determination of the molar ratio for the formed complex HPHMAB- Co^{2+}

Prepared according to method Jop [10,9] and modified by Vosburgh [11] a series of complex solutions where the L concentration is changed regularly with the persistence of the studied electrolyte concentration constant and the absorbance is measured in terms of the molecular concentration associated with the molecular concentration of the studied electrolyte.

Figure (7) shows the relationship for the studied cobalt concentrations (II). It is observed from the figure that there is a single refractive point on the two curves corresponding to a mole ratio of 4 and that the complex formed from the shape $Co(HPHMAB)_4$

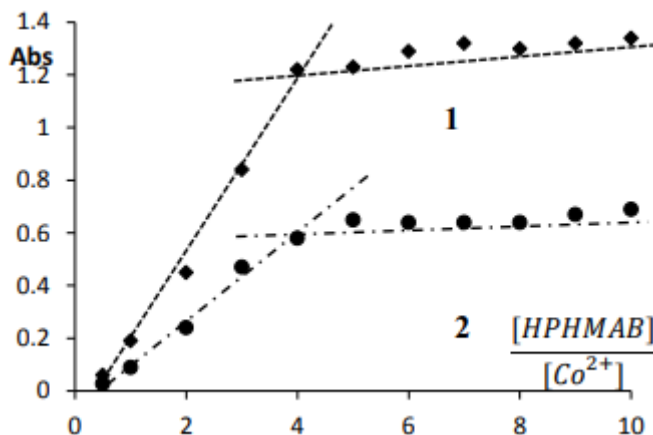


Figure 7: absorption of the HPHMAB- Co^{2+} complex according to the molar ratio method.
 (1) $[Co^{2+}] = 6.78772 \times 10^{-5} M$, (2) $[Co^{2+}] = 3.39384 \times 10^{-5} M$, $pH = 10$, $\lambda_{max} = 430 \text{ nm}$, $T = 50^{\circ}C$, $t = 5 \text{ min}$.

10. The Calibration curve for determination of Cobalt (II) Using HPHMAB reagent

The linear domain of the cobalt (II) concentration that achieves the Pierre-Lambert law was determined in order to selectively identify it using the HPHMAB reagent taking into account all the ideal conditions previously studied. Figure 8-a shows the best straight line obtained in the smallest squares method. It follows from the figure that Pierre-Lambert's law is within the domain (0.1-4) mg / l. This corresponds to a mole concentration of (0.16969-6.78768) 10^{-5} M and that the best straight line equation is of the form $A = m.c$, and that the correlation coefficient $R^2 = 0.9977$, thus the Pierre-Lambert law achieves an excellent degree within the field adopted for this study.

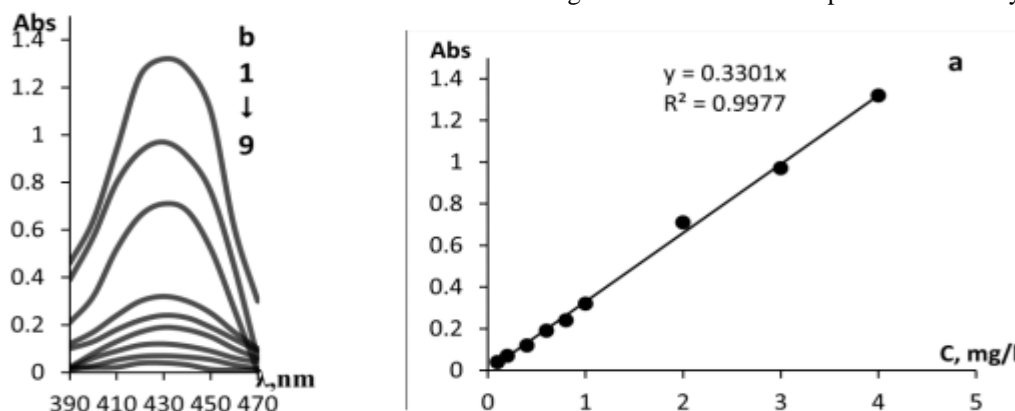


Figure 8: Standard cobalt (II) determination curve using the HPHMAB reagent
a- The relationship between absorption of the complex and cobalt(II) concentration

b. Complex spectroscopy at increasing concentrations of cobalt (II)

$C_{Co^{2+}}$, mg/l: 1(4), 2(3), 3(2), 4(1), 5(0.8), 6(0.6), 7(0.4), 8(0.2), 9(0.1).

[HPHMAB] = 6.78768×10^{-4} M, pH=10, T=50 °C, t=5 min, $\lambda_{max} = 430$ nm.

11. Effect interference ions

Table 3: Impeding and non-blocking ions and percentage of ions affecting complex formation

interference ions			Non-interference ions
1:4	1:2	1:1	
Mn ²⁺ , Pb ²⁺ , Ca ²⁺ , Fe ²⁺ , Ba ²⁺ , Al ³⁺ , Fe ³⁺	Cd ²⁺ , Cu ²⁺ , Zn ²⁺ , Cr ³⁺	Zr ⁴⁺ , NO ₃ ⁻ , Ni ²⁺ , Mg ²⁺ , Ag ⁺	Na ⁺ , K ⁺ , HPO ₄ ⁻ , CH ₃ COO ⁻ , Cl ⁻ , PO ₃ ³⁻ , NH ₄ ⁺ , I ⁻ , Cu ¹⁺

12. Statistical study of the proposed analytical method

Table 4: Analytical statistical results to estimate the validity and accuracy of the proposed spectral method for determination of cobalt (II)

pH=10, $\lambda_{max} = 430$ nm, n=3, $\alpha = 0.95$, T = 50 °C, t= 5min. Percentage of britton buffer 4%.

CL _{95%} , mg/l	ASE, mg/l	R%	RSD%	SD, mg/l	C _{Ni²⁺} , mg/l	
					C _{found}	C _{taken}
0.093±0.007	0.0015	93	2.85	0.003	0.09	0.10
0.213±0.014	0.0033	106.7	2.71	0.006	0.21	0.20
0.025±0.39	0.0058	97.5	2.57	0.01	0.39	0.40
0.607±0.038	0.0088	101.2	2.52	0.015	0.61	0.60
0.793±0.038	0.0088	99.1	1.93	0.015	0.79	0.80
1.023±0.038	0.0088	102.3	1.49	0.015	1.02	1.00
2.01±0.066	0.0153	100.5	1.32	0.027	2.01	2.00
3.04±0.05	0.0115	101.3	0.66	0.02	3.04	3.00
4.067±0.052	0.012	101.7	0.51	0.021	4.07	4.00



13. Calculation of detection limit

According to the limit of disclosure from the following relationship [12]:

Where n the number of points selected from the standard curve and the standard curve b and the student factor at a confidence level of 95% and S_0^2 is a contrast coefficient expressed in the following relationship:

$$S_0^2 = \frac{\sum(A_{exp} - A_{cal})^2}{n - 2}$$

Where A is the practical absorbance and Acal is the calculated absorbance of the standard curve relationship.

Table 5: Spectral and Analytical Properties of the formed Complex

britton 4%	Buffer Type percentage
10	PH
30	Time required to form complex, accurate
50	Temperature, °C
5	Heating time min
1	Complex Stability Time, Day
Pale yellow	Reagent Color
Yellow Orange, 430	Complex color and λ_{max} , nm
1:4	molar ratio Co: HPHMAB
$(0.16969-6.78768) \times 10^{-5}$	Linear analytical range, mol / l
(0.1-4)	Linear analytical range mg / l
0.3301	slope
0.9977	Correlation Coefficient
$1.4762 \times 10^{+4}$	Molecular absorption coefficient (Schwarzenbach) $l \cdot mol^{-1} \cdot cm^{-1}$
2.746×10^3	Fixed form a complex, k_{β}
0.05	Detection limit, mg / l

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