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(RESEARCH ARTICLE)

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Synthesis and characterization of new Thiocarbohydrazone reagent for flow injection spectrophotometric measurement of Co (II) ion an analytical sample

Hussein Ali Al-Bahrani *, Abdulmutalb BM Al-Khaleeli and Mohammed Nawfal Abdul Maged

Department of Chemistry, College of Education for Pure Sciences, University of Kerbala, Iraq.

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Abstract

A sample (analyte) is injected into a continuous flow of a carrier solution, where it mixes with chemicals before reaching a detector. This is done automatically using Flow Injection Analysis (FIA). A brand-new thiocarbohydrazone was made by mixing one amount of Methyl thiophen-Thiocarbohydrazone with two amounts of 5-methylthiophen-2-carboxaldehyde in ethanol, We used 1H NMR, 13C NMR and mass spectrometry to figure out the structure of the chemical we made. The FIA method was used to find Cobalt (II) ions in different samples by using this chemical as a spectroscopic reagent, Accurately finding cobalt is very important for environmental and health studies because it is an important element used in many biological and industrial processes.

Keywords: Methyl thiophen-Thiocarbohydrazone; hydrazine-1-carbothiohydrazide; flow injection; Thiocarbohydrazone; Cobalt (II).

1. Introduction

In the area of analytical chemistry Flow Injection Analysis (FIA) is a new and important method. An analyte-containing liquid sample is injected into a constant flow of a reagent. This is a simple but effective way for it to work [1-3]. The sample is moved through a number of tubes and analytical cells by this flow. In these, the chemical reactions that are needed to find out the chemical properties of the target compounds or to measure their concentration take place. [4-6] Automation technology is used by FIA to speed up the research process, which takes a lot less time than traditional methods. The main benefit of this method is that the moving stream mixes the sample and reagent quickly and effectively which leads to accurate results while using as few samples and chemicals as possible [7-9]. For example FIA works great for checking small amounts of samples that need to be done quickly or often, like samples from the environment, food, and medicine[10–9].

One of the best things about Flow Injection Analysis is that it can do more than other analytical tools in a number of ways. Some of these are quick reaction times, the ability to analyze a lot of samples in a short amount of time lower error rates due to automation and the ability to easily combine with other analytical methods like spectrophotometry. FIA can also be used to measure a lot of different chemical compounds and substances which makes it an essential tool in labs that need to be very accurate and efficient [10–12].

To sum up Flow Injection Analysis is a strong and useful analytical chemistry tool that lets scientists do quick, accurate and repeatable studies with little material. This makes it more useful in many areas like medicine farming, and business [15–18]. Cobalt is an important part of living things because it is a part of vitamin B12. It is also used a lot in making batteries and alloys so it needs accurate chemical methods to be measured [13–15].

* Corresponding author: Hussein Ali Al-Bahrani

2. Material and method

2.1. Apparatus

A 10 µl flow cell from Cecil was utilized in conjunction with a Shimadzu 120 UV-VIS spectrophotometer. The measurement of omax was carried out using a Shimadzu 1650 PC UV-VIS double beam spectrophotometer. The carrier fluid was transported using a peristaltic pump (Gilsason minipuls (2)) fitted with flexible polyvinyl chloride tubes with an internal diameter of 0.8 mm.Using a tow-channel manifold (Figure.1), using FIA spectrophotometer. The Rheodyne -USA injection valve was utilized to administer standard solutions and samples at the proper injection volumes. The reaction coil R.C as used to combine the product with a stream of buffer solution. The final product was mixed with the stream of alkaline oxalate at point (y), following the the mixing of coil RC.

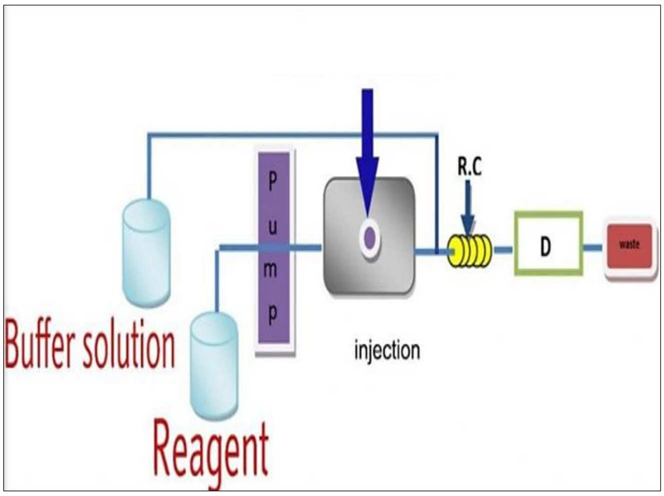


Figure 1 Manifold used to Co(II)ion using FIA Spectrophotometric Analysis

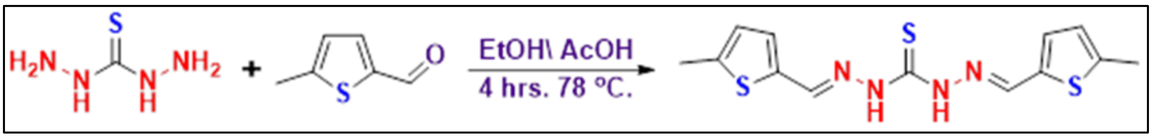
2.2. Reagents and Chemicals

All reagents and solvents were obtained from B.D.H., Fluka, and Merck with high purity, and no further purification was required.

2.2.1. Synthesis of 2-((5-methylthiophen-2-yl) methylene)-N'-(5-methylthiophen-2-yl- methylene) hydrazine-1-carbothiohydrazide

In round bottom flask (1 g, 9.42 mmole) of Methyl thiophen-Thiocarbohydrazone was dissolved in 25 ml of ethanol and 1 ml of glacial acetic acid with stirring, and (2.75 ml, 18.9 mmole) was added dropwise within 30 mins. Then the mixture was refluxed at 78 °C. for 4 hrs., the completion of reaction was choked by TLC, then the solvent was evaporated and the formed precipitate was filtered, washed with cooled ethanol, and dried at 60 °C. overnight to afforded 1.87 g of yellowed precipitate with 62% yield, m.p. 217-219 °C show as Scheme 1.

1H NMR (400 MHz, DMSO) δ 11.28 (s, 1H), 8.47 (s, 1H), 7.59 (d, J = 5.4 Hz, 1H), 6.97 (d, J = 5.1 Hz, 2H), 2.32 (s, 4H)show as Figure 2. 13C NMR (126 MHz, DMSO) δ 179.89, 145.02, 131.16, 129.66, 128.27, 127.67, 124.09, 18.07 show as Figure 3. m\z 323.2, theoretical 322.46 show as Figure 4.



Scheme 1 Synthesis of the reagent

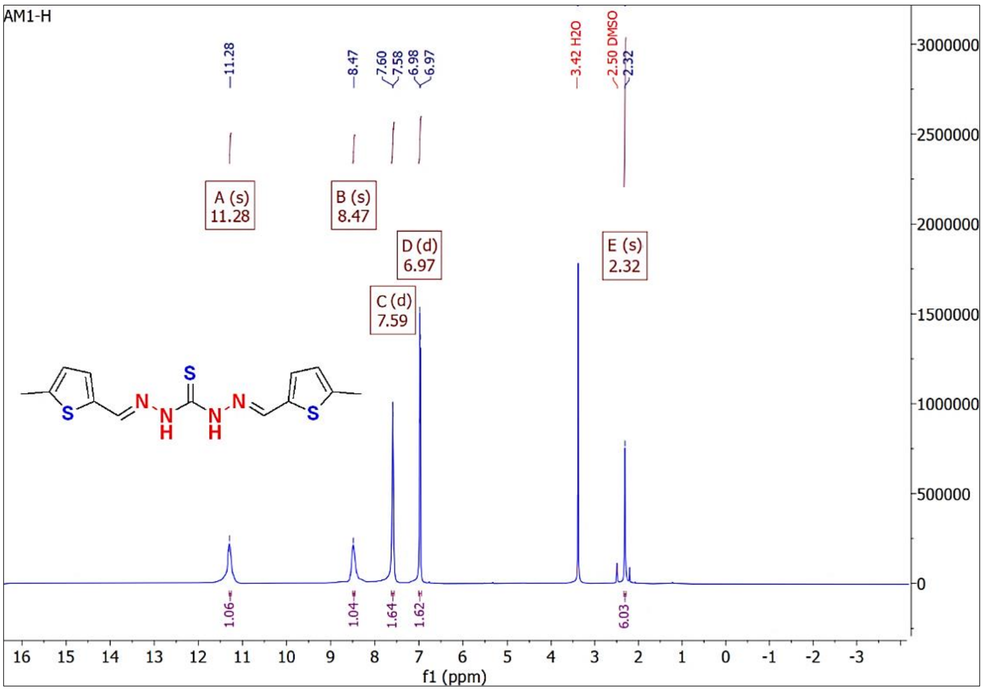


Figure 2 ^{1}H-NMR spectrum of the reagent

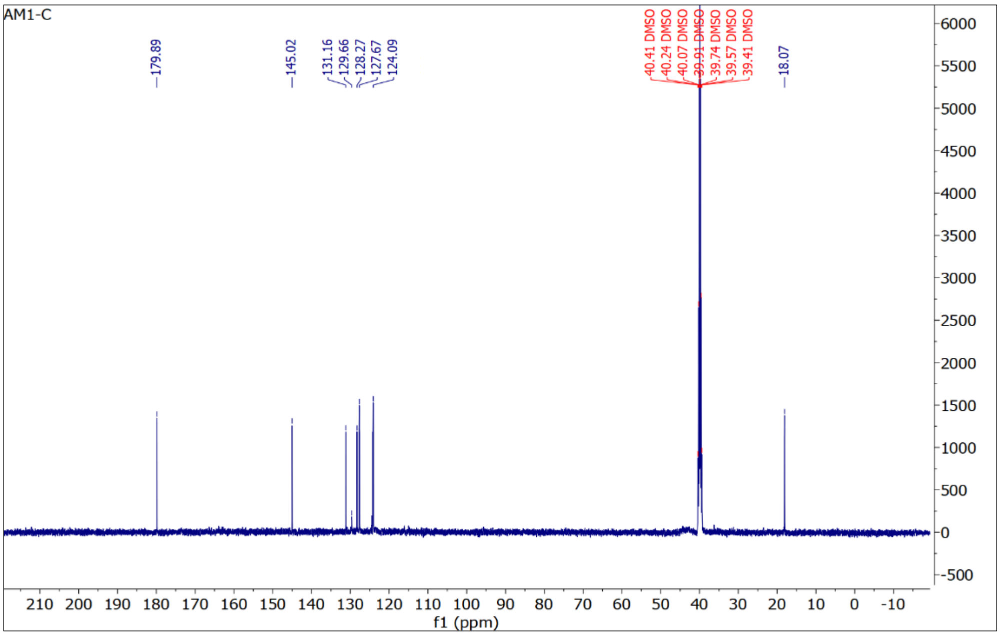


Figure 3 ^{13}C-NMR spectrum of the reagent

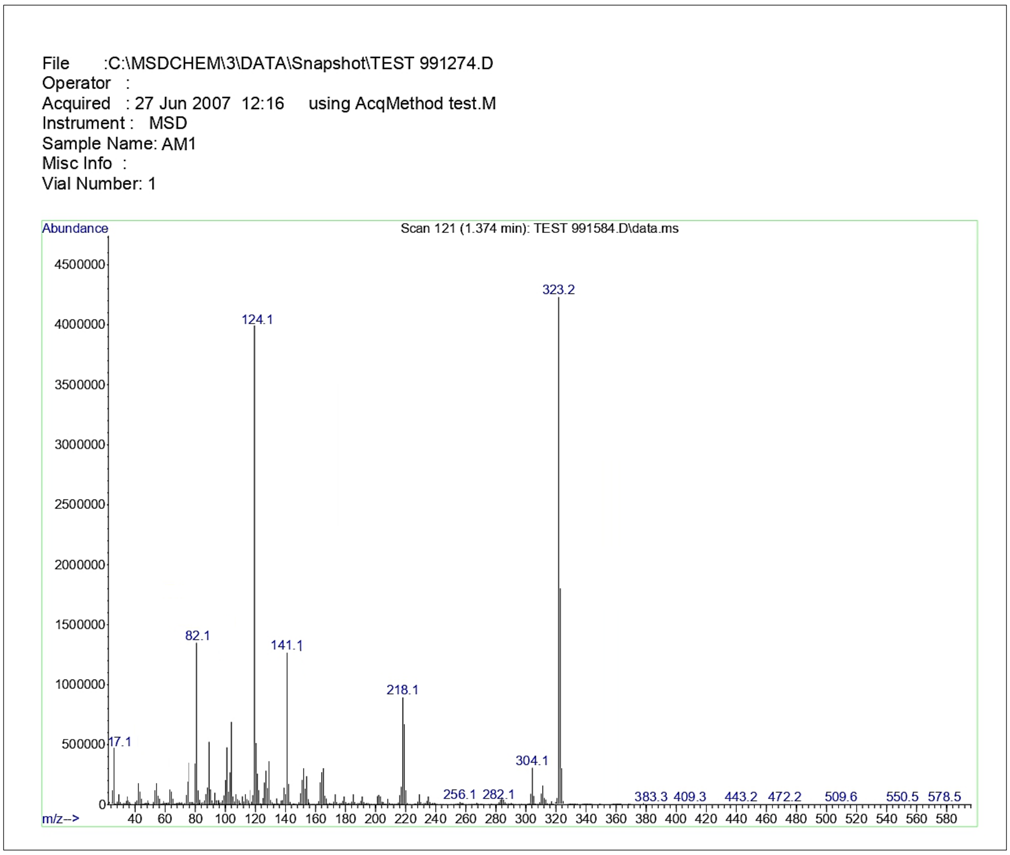


Figure 4 Mass spectrum of the reagent

2.3. Product Description

UV-Vis was used to characterize the synthesized reagent and complex products that were recovered from the process, and FT-IR and ^{1}HNMR spectra were obtained for the novel reagent.

2.4. Procedure for the FIA method

A 100.00µl sample is injected into a stream of 1×10^{-5} reagent solution at a rate of 0.60 ml/min. the stream is allowed to combine with another stream of (pH=6) solution in a 50 cm reaction coil. Next, a valve was injected mixture is passed while sustaining the reaction, and absorbance is gauged at 340.nm.

3. Results and Discussion

3.1. Effect of Reagent Concentration

Conc.	Abs
0.0004	0.308
0.0003	0.337
0.0001	0.326
0.00005	0.311
0.00003	0.290
0.00002	0.281
0.0001	0.326

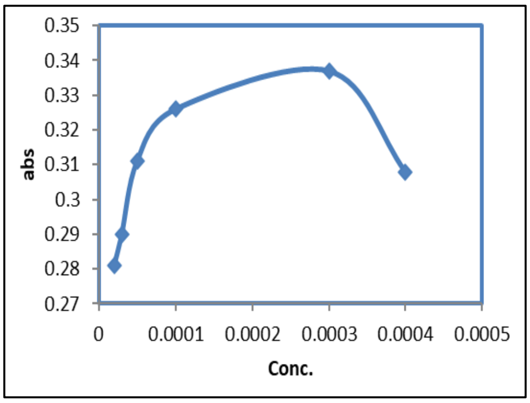


Figure 5 Effect of Reagent Concentration

3.2. The effect of the length of the interaction file

R.C	Abs
25	0.257
50	0.321
75	0.237
100	0.232
125	0.202

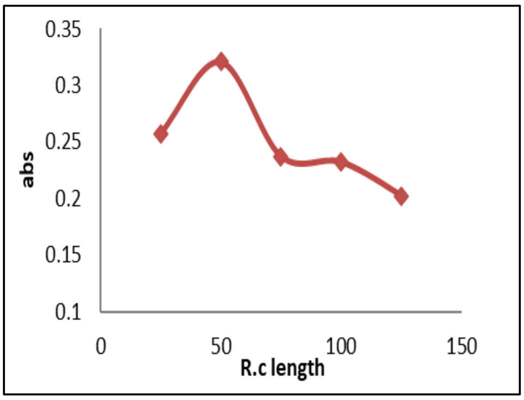


Figure 6 The effect of the length of the interaction file

3.3. Effect of screw size

loop	Abs
30	0.228
50	0.271
100	0.32
150	0.221
200	0.108

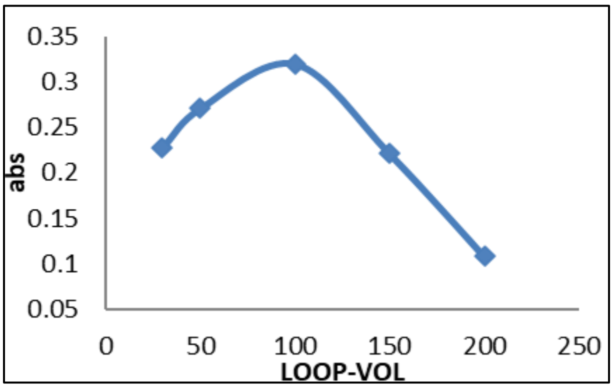


Figure 7 Effect of screw size

3.4. Effect of Rate

Rate	Abs
10	0.112
20	0.123
30	0.241
40	0.330
50	0.212
60	0.201

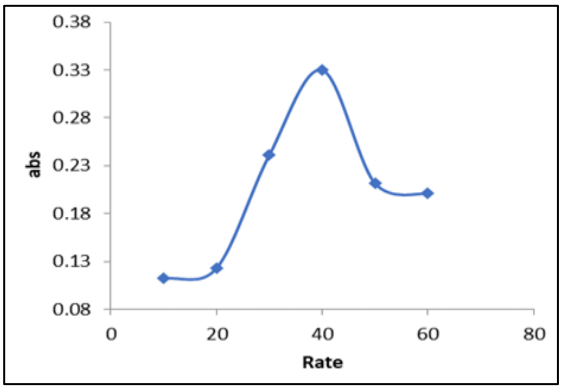


Figure 8 Effect of Rate

3.5. Calibration Curve for Complex in Co (II) ion

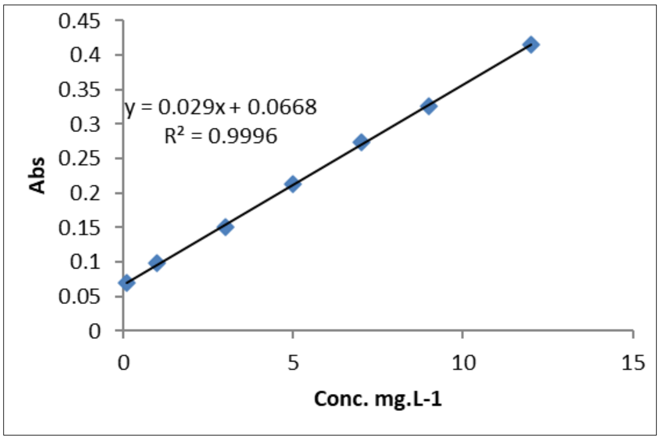


Figure 9 Calibration Curve for Complex in Co (II) ion

It was used for basic studies of the reaction between Cobalt complex (II) and ligand (Methyl thiophen-Thiocarbohydrazone). Something Prussian blue was made in an acidic medium. Figure 10 shows that the color absorbs the most light at λmax 500 nm.

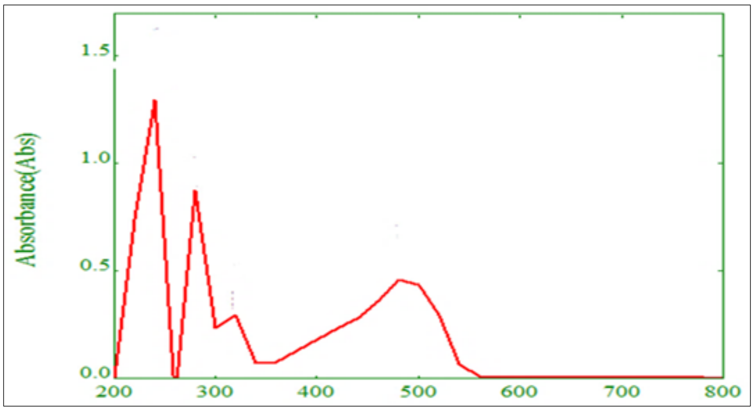


Figure 10 Absorption spectrum of Cobalt complex (II) with ligand (Methyl thiophen-Thiocarbohydrazone)

For the batch method, the effect of Cobalt ion (II) concentrations from 1x10-4 to 7.5x10-5 M was tested, and it was found that 1x10-4 M gave the best results. The effect of ferric chloride solution concentrations from 0.5x10-3 to 7x10-3 was also tested, and 5x10-4 gave the best results. It changes color when Cobalt complex (II) binds to a ligand called Methyl thiophen- Thiocarbohydrazone. We looked at what happened when we added different amounts of ammonium hydroxide (0.01–0.5M) along with 5x10-3 M 4-AAP and 5x10-3M cobalt chloride solution. The best absorbance was seen at a concentration of 0.1M, so that was picked for further use (Fig. 11).

The effect of the change in the reaction coil length has been studied in the range (50 -125) cm, and the system conditions are: $CoCl_2.2H_2O$ concentration is 1 × 10-5M and the concentration of Methyl thiophen-Thiocarbohydrazone reagent is 1 × 10-5M M The PH The regulator Buffer solution is 9 and the cell size is 10 µL loaded in the typical model loading link and the flow velocity of the first and second carrier current is 2.1 ml. min-1 and the maximum wavelength for Cobalt is 500nm.

The effect of the change total flow-rate within the range (0.4 -2.8) ml / min was studied, and the system conditions are: The concentration of $CoCl_2.2H_2O$ is (1×10^{-5}) M and the concentration of the Methyl thiophen-Thiocarbohydrazone reagent is (1×10^{-5}) M The acidity of the buffer solution is 9 and the cell size is 10 µL Loaded in the model link and the flow velocity of the first and second load current is 2.1 ml.min-1 and the maximum wavelength for Cobalt is 500nm, Figure (12) It shows the results obtained.

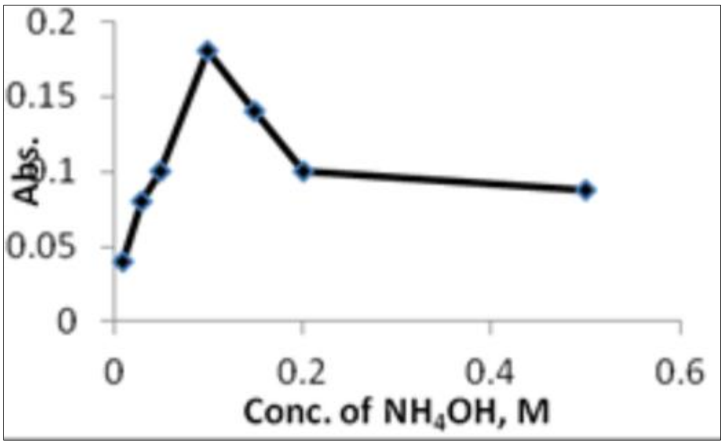


Figure 11 Effect of NH_4OH concentration

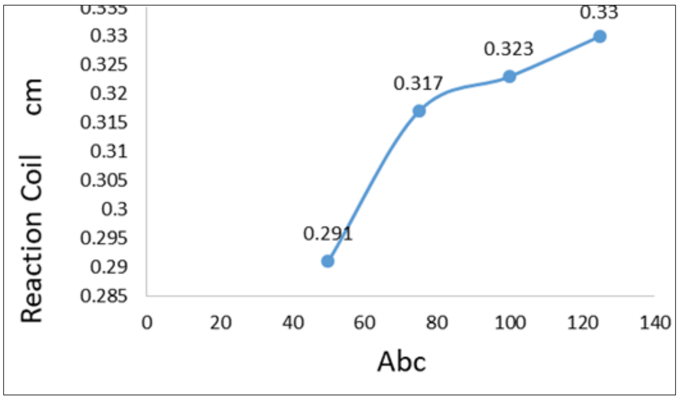


Figure 12 Effect of reaction coil length

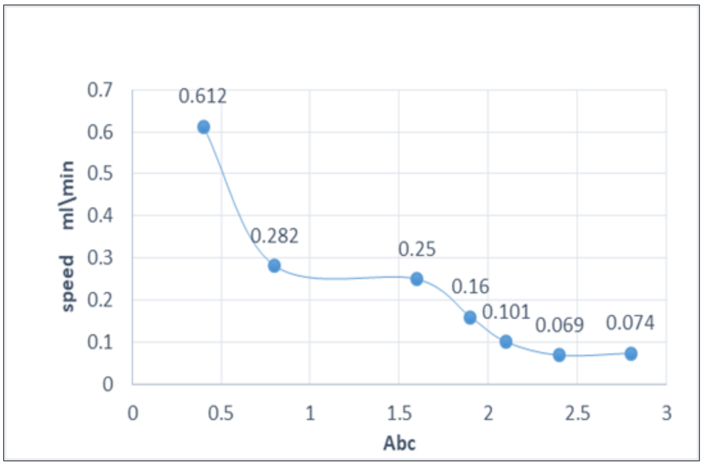


Figure 13 Effect of total flow-rate

While results showed in Fig (14) A loop has been used in a pump with a steel metal of different lengths of different sizes (50 ml - 250 ml) passing the current carrier detector and the buffer solution with a pH equivalent to 9 at a fixed concentration 1 * 10-4 and absorbing readings for each length by means of a 10 ML spectrometer.

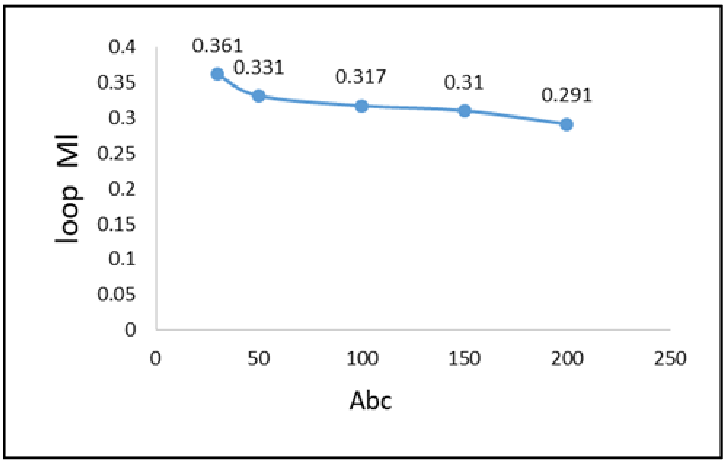


Figure 14 Effect of loop volume injected

Figure 15 displays the calibration curves that were made under the best conditions for the Cobalt complex (II) with ligand (Methyl thiophen-Thiocarbohydrazone). found by using both of the methods we talked about earlier. The statistical numbers are summed up.

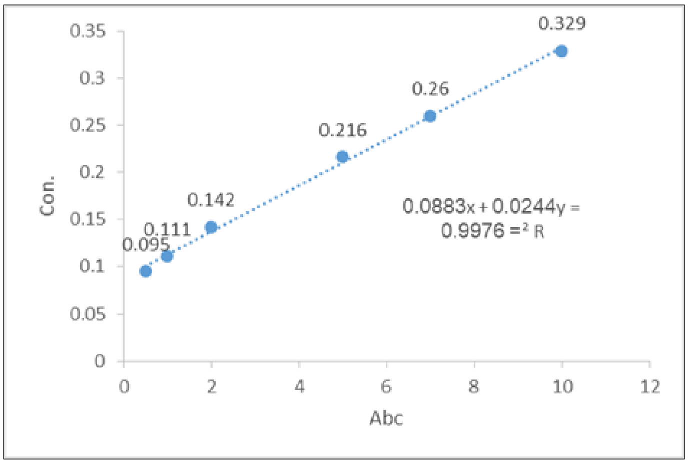


Figure 15 Typical calibration curve for Cobalt ion (II) with ligand (Methyl thiophen-Thiocarbohydrazone). using FI-method

4. Conclusion

The developed FIA method successfully determined Co (II) ion concentrations with high precision and efficiency. The synthesized thiocarbohydrazone reagent proved to be a reliable spectrophotometric agent for cobalt analysis. Given cobalt's significance in industrial and biological processes, this method offers a valuable approach for its rapid and accurate detection. The study highlights the potential of FIA for rapid, automated, and accurate chemical analysis, making it a valuable technique for various analytical applications.

Compliance with ethical standards

Disclosure of conflict of interest

No conflict of interest to be disclosed.

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