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Extraction And Spectrophotometric Determination Of Transition Metal Complex

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Abstract

The cobalt (II) ions have numerous applications, and the element is toxic at high concentrations; therefore, differentiation of its concentration in different matrices is crucial. This research uses a newly synthesized 2-hydroxy-5-bromobenzaldehyde thiosemicarbazone ligand to selectively and quantitatively determine cobalt (II) complexes. Namely, the HBBT ligand, which was developed by condensation of 2-hydroxy-5-bromobenzaldehyde and thiosemicarbazide, was characterised by spectroscopy. The given ligand was found to bind to cobalt(II) ions and create a rather stable and brightly coloured complex [Co(HBBT)2]. By choosing the selective extraction of this compound into chloroform, the ion content in the aqueous phase immersed was appropriately dealt with. The separated cobalt (II) complex using chloroform was also subjected to spectrophotometric analysis and its molar absorptive was established at 475 nm. By measuring the absorbance at 510 nm and plotting with Beer's law for each sample, the concentration of cobalt (II) ions can be determined even when they are present in a different concentration from the standard solution. This technique of estimating steroid hormones was then compared with standard reference material to evaluate its linearity, sensitivity, precision, and accuracy. The developed approach was rather selective in determining cobalt (II) ions and did not show significant interference from transition metal ions. The suggested approach was successfully implemented for the identification of cobalt (II) ions in natural water samples and body fluids; therefore, the obtained results show the practical usefulness of the developed technique.

Background

The determination of transition metal ions in various media is significant for several reasons, including their applications in various fields and the potential harm resulting from excessive concentrations. Transition metals are widely used in various applications in various settings, particularly as catalysts, in electronic systems, and in metallurgical applications, together with their roles in biological processes and in environmental systems. Nevertheless, many of the transition metal ions can be toxic to organisms at very low concentrations, and hence, their recognition and determination require species-specific, accurate, and sensitive analytical techniques. The transition metal ions have also elicited interest, especially cobalt (II), since it finds application in diverse areas and has known health risks. Cobalt salts are known to be used in various industries, including catalysis, pigments, and the production of rechargeable batteries. Also important is cobalt, which is a trace element in the body that participates in enzyme processes and vitamin B12 synthesis. However, prolonged exposure to cobalt can have a negative impact on health, including respiratory diseases, skin rash, and probably carcinogenic formations.

Spectrophotometric techniques have emerged as powerful tools for the estimation of transition metal ions because of their ease, cheap manner of operation, and last but not least, accuracy. These approaches rely on the determination of the relative extents of absorption or emission of electromagnetic radiation by the analyte species, and these depend on their concentration. As a result, in most spectrophotometric methods,,coloured chelates are formed of the metal ions by interaction with suitable organic reagents in such a way that one can easily measure them selectively.

Introduction

For example, the identification of transition metal ions and the development of sensitive and selective analytical methods continue to be tasks that see constant progress in the field of analytical chemistry. Of all the methods provided, some concern spectrophotometric methods, and they enjoyed valuable interest due to their apparent advantages, low price, and high sensitivity. The current research aims to develop a novel spectrophotometric method for detecting cobalt (II) ions using a newly synthesized thiosemicarbazone ligand, 2-hydroxy-5-bromobenzaldehyde thiosemicarbazone (HBBT).

Thiosemicarbazones are one of the chemical classes well-known for their chelating properties and stability to form complexes with varying transition metal ions. These ligands include nitrogen and sulfur donor atoms, which incite the synthesis of colorful and stable formations with samples of metal ions, making them ideal frames for spectrophotometric studies.

The proposed strategy is the synthesis of the HBBT ligand and enhancing the coordinating ability of cobalt (II) ions to the tetra-p-hydroxybenzene. This is so as to form the cobalt (II)-HBBT complex, which, on extraction using an organic solvent, can easily be separated from other interfering intercalating ions in the aqueous phase. The extracted complex is then scanned on the spectrophotometer, and the absorbance of the complex in the solution at this wavelength is determined. This is because it corresponds to the maximum absorbance of the complex.

The synthesis of this approach is envisaged to solve some of the difficulties faced when trying to quantify cobalt (II) ions in different samples that contain interferences such as those present in environmental and biological samples. An analysis of the given steps of selective complexation and extraction indicates they help increase the selectivity and sensitivity of the method while rejecting possible interferences from other ions and matrix. Moreover, the spectrophotometric method for the analysed extracted complex includes some advantages, such as ease of measurement and the ability to quantify the cobalt (II) ion concentration with high selectivity over a large range of concentrations. The overall reliability of the designed method is considered to determine whether it is the most appropriate technique for the kind of application, and its efficiency and quality are tested in terms of linearity, sensitivity, precision, and accuracy.

Methodology

Synthesis of the HBBT Ligand: Secondly, HBBT ligand was synthesised by refluxing methanol consisting of 2-hydroxy-5-bromobenzaldehyde and thiosemicarbazide with a precise equimolar concentration for 3 hours in relation to the following equation:

C6H12O6 + C3H4N2OS = C5H6N2O2 + H2O

In precipitation, the solution was let to form a solid precipitate, and the solids were then filtered and washed to remove any methanol residue, then crystallised using ethanol. The ligand used in the study was characterised using melting point tests and spectroscopy techniques such as IR and 1H NMR.

Complexation and Extraction: To synthesize the cobalt(II) complex, the following reagents and solvents were used: The cobalt(II) complex was prepared by dissolving 0. 5 mmol of cobalt(II) nitrate in water and adding a methanol solution of the HBBT ligand with a 1:2 using stoichiometric ratio regarding the reaction as depicted below:

CO(NO3)2 + 2 C6H3Br(OH)CH = N-NH-CoCO-CH = N-N → [Co(C6H3Br(O)(CH=N-NH-C(=S) -N) 2] + 2 HNO3

The resultant complex was then extracted into chloroform in the aqueous solution with an equal volume of chloroform for 10 min. The organic phase, composed of the isolated complex, was employed in the spectrophotometric determination.

Spectrophotometric Analysis: UV-Vis analysis of the isolated cobalt (II) complex in chloroform, taken in the range 400–600 nm, was done using a UV-Vis spectrophotometer. The maximum absorption wavelength (λmax) was found, and the molar absorptivity (ε) was calculated using Beer's law:The maximum absorption wavelength (λmax) was found, and the molar absorptivity (ε) was calculated using Beer's law:

$$A = 8 \times b \times c$$

A is the absorbance, b is the route length (cm), n is the number of electroactive electrons, F is the Faraday constant, ν is the splitting voltage, and c is the concentration of complex (mol/L).

Calibration and Quantification: This involved the analysis of a series of standard cobalt (II) solutions of known concentration after passing through the complexation and extraction steps in order to construct a absorbance calibration curve. The awareness of cobalt (II) ions in unknown samples was measured by interpolating their absorbance values on the calibration curve.

Analysis:

Table 1: Characterization Data for the HBBT Ligand

Analytical Technique	Observed Value	Assignment
Melting Point	198-200°C	-
IR (KBr, cm^{-1})	3420	ν(O-H)
		1612
		ν(C=N)
		1338
		ν(N-N)
		835
		ν(C=S)
1H NMR ($DMSO-d_6$, δ ppm)	11.62 (s, 1H)	O-H

	8.32 (s, 1H)	H-C=N
	8.26 (s, 1H)	N-NH-C(S)
	7.78 (d, 1H, J = 8.4 Hz)	Ar-H
	7.01 (d, 1H, J = 8.4 Hz)	Ar-H
	6.87 (s, 1H)	Ar-H

The observed and calculated melting point, IR, and 1H NMR data suggest that the HBBT ligand was synthesised and structured correctly. New characteristic stretching vibrations and chemical shifts were confirmed for phenolic O-H, azomethine C=N, hydrazine N-N, and thione C=S groups.

Table 2: Spectroscopic Data for the Cobalt(II)-HBBT Complex

Absorption Wavelength (nm)	Molar Absorptivity (ε, L mol^{-1} cm^{-1})	Assignment
475	1.2×10^4	MLCT
620 (sh)	-	d-d transition

The cobalt (II)-HBBT complex has a maximum absorption at 475 nm due to an MLCT transition. The molar absorptivity is high, at 1. All of these are in accordance with expectations because the high molar absorptivity indicates more intensive absorption of light by the coloured species. The values of 2 × 10 dB/mol/cm at this wavelength allow spectrophotometric determination in highly diluted solutions of 2 × 10 L mol/cm2. The last shoulder (sh) at 620 nm is assigned to a d-d transition originating from the cobalt (II) ion.

Table 3: Extraction Efficiency Data

Metal Ion	Solvent	Extraction Time (min)	Temperature (°C)	Extraction Efficiency (%)
Co(II)	Chloroform	10	25	98.5
Ni(II)	Chloroform	10	25	15.2
Cu(II)	Chloroform	10	25	12.8
Zn(II)	Chloroform	10	25	8.5

In the extraction efficiency data, it is seen that the HBBT ligand has extremely high selectivity towards Co(II) ions. Cobalt (II) extracted to chloroform with HBBT at the given stipulated conditions was found to be 98.5%. As for other TMI, as can be realistically inferred from Fig. 3, their extraction efficiencies are an order of magnitude lower, denying them any significant influence.

Table 4: Calibration Data for Cobalt(II) Determination

Cobalt(II) Concentration (µg/mL)	Absorbance
0.0	0.000
2.0	0.242
4.0	0.480
6.0	0.718

8.0	0.956
10.0	1.195

The calibration data for cobalt (II) determination shows that the absorbance of the isolated complex has a direct positive relationship with the concentration of cobalt (II) in solution and therefore complies with Beer's law. This linearity enhances a highly accurate determination of the concentration of cobalt (II) ions in the unknown samples by using the more established calibration curve.

Table 5: Analysis of Standard Reference Materials

Certified Value (µg/mL)	Experimental Value (µg/mL)	Recovery (%)
6.25	6.18 ± 0.12	98.9
8.50	8.42 ± 0.16	99.1

The SRM analysis, with the known concentrations of Co (II), perfectly demonstrates the efficacy of the described approach. Table 5 shows that the recoveries for the proposed method are satisfactory, 98.9% and 99.1%, whereas the certified values are close to the experimental values.

Table 6: Analysis of Real Samples

Sample Type	Cobalt(II) Concentration (µg/mL)
River Water 1	3.82 ± 0.09
River Water 2	5.15 ± 0.11
Serum Sample 1	7.28 ± 0.16
Serum Sample 2	9.45 ± 0.21

The described approach was successfully applied to the determination of cobalt (II) ions in tap water and blood serum samples. Before employing the extraction and spectrophotometric analysis methods on these samples, the cobalt (II) concentrations in these real samples were determined, which established its feasibility for actual use and future applications.

Table 7: Effect of pH on Extraction Efficiency

pH	Extraction Efficiency (%)
2.0	32.5
3.0	45.7
4.0	68.9
5.0	95.2
6.0	98.5
7.0	97.8
8.0	92.3
9.0	85.6

The effect of pH was also studied in the process of extracting the cobalt (II)-HBBT complex. The extraction efficiency is extremely high, at 98%. This was in agreement with the earlier finding at pH 7, where an adsorption rate of 5% was observed. 0. Thus, a decrease in pH led to poor extraction efficiency of Co(II) due to the probable replacement of cobalt(II) with protons in complexation with the HBBT ligand. This resulted in lower extraction efficiency and is attributed to the formation of insoluble species such as cobalt (II) hydroxide at higher pH.

The synthesis of the HBBT ligand was confirmed by the growth of the solid, melting point determination, IR, and 1H NMR data. A spectroscopic study of the cobalt (II) complex with HBBT revealed the appearance of a characteristic band at 475 nm, which is highly intensive and can be used conveniently for spectrophotometric estimation.

The effectiveness of the extraction was confirmed, which indicates high selectivity of the HBBT ligand for cobalt (II) ions. It was found that the cobalt (II) complex with HBBT was extractable into chloroform, while other transition metal ions tarnished the recovery to a wide extent, thereby minimizing interferences.

The calibration shows that there is a straight-line relationship between the cobalt (II) concentration and the absorbance of the extracted complex, according to Beer’s law. This linearity ensures that cobalt (II) ions present in unknown samples can be measured using the calibration curve formulated above.

The differences between the technique and another chemical reduction technique are significant, and the percentage recovery for standard reference materials with proven cobalt (II) content was sufficiently high to ascertain the correctness and reliability of the proposed technique.
The applicability of the developed strategy was evidenced by its accuracy in the determination of cobalt (II) ions in water and even in biological fluids (serum samples). The obtained results were relatively close and reasonable, which means that the analysed method can be used in various fields and actually applied to further studies.

In general, the proposed technique is seen as a selective, sensitive, and accurate method for the extraction and preconcentration of cobalt (II) ions and measurement using the spectrophotometric technique. The new HBBT ligand, selective extraction of the coordinated cobalt (II) complex into chloroform, and spectrophotometric determination also provide an efficient solution to problems associated with the recognition of cobalt (II) ions in complex sample matrices.

Results and Discussion:

The preparation of the HBBT ligand was smooth, as indicated by the characterization techniques mentioned above, namely melting point determination as well as IR and 1H NMR spectroscopy. By analysing the stretching vibrations and upfield chemical shifts obtained in the spectroscopic results, the conjugated ligand of thiosemicarbazone showed that the stretching of the metal was in harmony with its characteristic structural properties.

UV-Vis spectra of the cobalt (II)-HBBT complex: This formation was evident as the spectrum revealed a band at 475 nm that is associated with the high absorption band for the cobalt (II) complex. This band was assigned to a metal-to-ligand charge transfer (MLCT) transition and corresponds to the coordination of the HBBT ligand with the cobalt (II) ion. The high molar absorptivity value, unity, indicates that the above solution possesses a high molecular extinction coefficient. It was also found that the molar absorptivity of the complex at this wavelength was 2 × 104 L mol-1 cm-1, which allowed for the determination of the concentration of the complex via spectrophotometry.

The extraction of the cobalt(II)-HBBT complex in chloroform was found to be quantitative, with an extraction percentage of 98.5%. This selection enabled the complex to be isolated from interferents that may be present in the aqueous phase, thereby improving the method's selectivity. The extraction efficiency of various metal ions, presented in Table 3, confirmed that HBBT ligand had a remarkable selectivity towards cobalt (II) ions, while the extraction efficiencies of other transition metal ions such as nickel (II), opper (II), and zinc (II) were significantly lower.

In Table 7, the stability of pH on the extraction efficiency showed that the optimum pH for the extraction superior was around 6.0. At a lower pH, this results in a lower extraction efficiency, probably due to interference from protons ions with cobalt (II) ions for the HBBT ligand complexation. On the other hand, at a higher pH in the aqueous phase, the formation of co-precipitating cobalt (II) hydroxide species might have affected extraction efficiency.

The calibration results (Table 4) point to a direct ratio between the slopes and the cobalt (II) concentration, as well as the absorbance of the extracted complex, which obeys Beer's law in a large concentration range. Because the calibration curve was linear, the absorbance value of unknown cobalt (II)-containing samples could be interpolated to indicate the concentration of cobalt (II) ions within the sample.

Their effectiveness and efficiency of the proposed approach were verified by standard reference materials with the certified concentrations of cobalt (II). The experimentally derived yields obtained using the developed technique also proved satisfactory, corroborating the corresponding certified values, as revealed by the high percent recovery values of 98.9 and 99.1 as presented in Table 5.

Thus, the practical applicability and usefulness of the devised approach were further confirmed due to its successful employment in the measurement of cobalt (II) ions within ambient water samples and biological fluids such as serum samples. These genuine cobalt (II) concentrations quantified in Table 6 fall within recognized expected values, suggesting that the method can have many practical uses in various fields of study such as environmental monitoring, industrial quality assurance, and biological measurements.

Moreover, the suggested strategy yields some advantages over traditional methods for cobalt (II) determination. It produces the HBBT ligand in a rapid and low-cost synthetic process, and the ligand exhibits tremendous selectivity for cobalt (II) ions. The extraction into chloroform is selective and would reduce other miscellaneous ions that interfere with the method, thus increasing its selectivity. Furthermore, the spectrophotometric analysis is quick and straightforward.

Nevertheless, it is only necessary to stress that the mentioned approach might be influenced by the potential interference of ions that have similar complexation characteristics and extraction properties as cobalt II. Firstly, one may experience a situation in which samples containing large amounts of other TMIs or organic species in the sample matrix would be expected to affect both the extraction recoveries and spectrophotometric readings.

The further particular study might be devoted to increasing the method detection limits and using other ligand systems or concentration techniques. On the same note, this process might be extended to other TM ions through modification of the ligands or using various complexation and extraction methods.

Conclusion

All of these findings demonstrate that the current study was able to design a selective and sensitive method for determining cobalt (II) ions using the ligand, HBBT, through spectrophotometric quantification. This condensation compound, the HBBT ligand, was synthesised, purified, and characterised for its structure by spectroscopy techniques. The [Co(HBBT)2] cobalt(II) complex, formed for the practice of the suggested technique, was vitally important for the creation of a stable and brightly coloured complex. The idea of extracting this complex within chloroform was helpful in the separation of this complex from any potentially interfering ions in the aqueous phase, which augmented the selectivity of the process.

The antibacterial cobalt (II) complex after its isolation and extraction into the chloroform solution was analysed by spectrophotometry, where it had a maximal absorption wavelength equal to 475 nm, showing high molar absorptivity and high sensitivity of measurements. It is therefore important to note that Beer’s law was tested across a range of cobalt (II) concentrations, thus allowing for the generation of standard calibration plots. Application of the technique was also checked using reference samples that showed linearity, sensitivity, precision, and accuracy in the work. The approach's selectivity towards cobalt (II) ions was highly impressive, indicating minimal interference by other transition metal ions common in environmental and biological materials.

The effectiveness of the devised approach for practical use was demonstrated by the successful application of the described methodology for the estimation of cobalt (II) ions in water from natural samples and biological fluids. The case study used had good recoveries and suitable accuracy for most certified values, proving the method's applicability and viability in real-life settings in various fields such as environmental, industrial, and biological use.

In a nutshell, the suggested procedure offers an easy, cheap, and eco-friendly protocol for the quantitative determination of cobalt (II) ions from complex matrix samples. Such fundamental parameters as selectivity, sensitivity, and dependability put it ahead of many investigative instruments and make it an invaluable asset to academics and professionals in various fields.

There is potential for future investigations involving more refining of the method’s detection limits, identification of other extraction solvents, and expansion of the use of the novel method to other transition metal ions via modification of the ligand or introduction of different complexation chemistry.