DETERMINATION OF COBALT (II)

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The main use of cobalt, are in important alloys, high strength and high temperature alloys cobalt compound are used in ceramic industries for the decolourisation of clay. Organic salts are used as driers for paints, ink and varnishes.

Cobalt is one of the most important traces essential for biological systems[1]. It is a constituent of cyanocobalamine (vitamin B12). It plays very important role in animal nutrition. Some cobalt deficiency diseases in animals are known. Animal suffering from cobalt deficiency usually shows marked important in the apatite and other conditions within three to seven days after cobalt is supplied.

Reagent for the spectrophotometric determination of cobalt have been developed by number of workers[2-4]. Nitroso[5] salts are used for determination of cobalt. Thiobenzoylacetone[-6] from a complex with cobalt (II) which can extracted in benzene as a colourimetrc reagent used for extraction and determination of cobalt is numerous[7-11].

It is obvious from above discussion that the study of the role of cobalt in various systems is very much dependent on the rapid method of its separation from other elements and its determination in traces quantities.

Procedure for Extraction of cobalt (II)

An aqueous solution containing 1 mg of cobalt, taken in a beaker, and mixed with 1 ml of 2M Ammonium chloride solution and 1 ml of 0.5% isonitrosothiocamphor in alcohol. The pH of the solution was adjusted up to the desire value, with dilute solution of hydrochloric acid or ammonium hydroxide, keeping total volume of 10 ml with purified water. The mixture was

transferred in a separating funnel and equilibrated for one minute with an equal volume of chloroform. The two phases are allowed to separated out.
The compound was analyzed as anal. Calcd. For C_{20} H_{28} $N_2O_2S_2Co$:
C 53.87%; H 6.28%; N 6.28%; S 14.08%., and Co 13.06%,
Found C 53.31; H 6.34%; N 6.16%; S 14.22%. and Co 13.10%

Procedure for Spectrophotometer determination of cobalt (II)

Mixed 1 to 50 mcg of cobalt, 1 ml of 2 M ammonium chloride and 1 ml of 0.5% Isonitrosothiocamphor in alcohol was added. The pH of solution was adjusted to 7 with the help of dilute solution of hydrochloric acid or ammonium hydroxide. The volume of solution maintained up to 10 ml & transfer this mixture into a separatory funnel. Mixed the content for one minute with 10 ml of chloroform. The organic layer was collected in a test tube and absorbance of same was taken at 400nm against reagent blank. The amount of cobalt is determined with a calibration curve.

The calibration curve was plotted by taking known amount of cobalt and followed the method described as above. The absorbance was plotted against concentration of cobalt.(Table 15)

Procedure for mole ratio curve:

A series of mixture containing fixed amount of cobalt & increasing amount of reagent in 1 ml of alcohol were treated as described in procedure of spectrophotometer determination of cobalt. Absorbance of such extract was measured at 400 nm using chloroform as a blank (Refer Table 16)

Stability of complex:

The extracted colour remain constant for more than 20 hours. (Refer. Table 17)

Effect of pH:

The maxima of colour was found only at 6.5 to 7.5, and it may be concluded that better results can be obtain at pH 7 (Refer. Table 18)

Results and Observation:

The percentage extraction of cobalt, increases with the rise of pH from pH 1 to 6 and maxima found at pH 7, and above 7.5 pH it was started to decreasing.

The colour in different solvent was observed was in the following order. (Table19)

Chloroform>Benzene>Carbontetrachloride>Toluene>Chlorobenzene.

Chloroform is selected for the extraction and spectrophotometric determination of Cobalt because it gives highest colour produce in chloroform.

Validation of Analytical Technique [12-14]

Parameter: The analytical procedure is prepared for the following parameter.

1. **Specificity:-** Specificity is carried out to check the interference due to diluents in analysis.

   Acceptance Criteria: The absorbance proves that there is no interference due to diluents indicating method is specific.

2. **Linearity :** Linearity is established by demonstrating that the results obtained, are directly proportional to that concentration. The Solution were prepared at different concentrations level and absorbance was measured.
   A graph of concentration v/s absorbance was plotted which is Linear.

3. **Accuracy:** Accuracy of the method was established by recovery experiment known amount of Cobalt was added at there different concentration and analysis was performed.

Sr.No.	Qty. added in ppm	Absorbance	Quantity recovered in ppm	% Recovery
1	0	0	0	--
2	40	0.552	39.94 ppm	99.85 %
3	50	0.693	50.14 ppm	100.28 %
4	60	0.833	60.27 ppm	100.45 %
Mean recovery.				100.19%

Mean recovery of 3 level is calculated, which is 100.19 and is in acceptable limit, indicating that method is accurate under the prescribed conditions.

4. Precision: Precision of the method was established by performing assay 3 time by same analyst.

Sr.No.	Conc. of Cobalt in ppm	Absorbance	% of Cobalt
1	50 ppm	0.692	100.14 %
2	50 ppm	0.693	100.21 %
3	50 ppm	0.690	99.85 %
Mean			100.06 %

Mean of 3 analysis is 100.06 % and is in acceptance limit, indicated that method is validated.

5. Robustness: The robustness is proceeded by obtaining the analytical results on the portion of same sample by different analyst.

Sr.No.	Conc. of Cobalt in ppm	Analyst	Absorbance	% of Cobalt
1	50 ppm	Analyst I	0.690	99.85 %
2	50 ppm	Analyst II	0.690	99.85 %
3	50 ppm	Analyst III	0.691	100.0 %
Mean				99.90 %

Mean of results of all three analysts is 99.90 % which is in acceptable limit, and indicated that the method is validated.

Table 15

Absorbance measurement of Cobalt in chloroform with the help of Isonitrosothiocamphor at different wavelength .

Concentration of Cobalt : 50 ppm

Volume of chloroform : 10 ml

Time of equilibrium : 1 min.

Sr. No.	Wavelength	Absorbance
1	350	0.593
2	355	0.588
3	360	0.581
4	365	0.586
5	370	0.561
6	375	0.552
7	380	0.572
8	385	0.588
9	390	0.606
10	391	0.610
11	392	0.610
12	393	0.636
13	394	0.654
14	395	0.667
15	396	0.670
16	397	0.680
17	398	0.688
18	399	0.689
19	400	0.691
20	401	0.690
21	402	0.690
22	403	0.685

Cont.

23	404	0.682
24	405	0.675
25	406	0.666
26	407	0.648
27	408	0.621
28	409	0.602
29	410	0.597
30	415	0.590
31	420	0.581
32	425	0.489
33	430	0.446
34	435	0.491
35	440	0.380
36	445	0.368
37	450	0.335
38	460	0.335
39	470	0.333
40	480	0.327
41	490	0.342
42	500	0.368
43	520	0.365
44	540	0.351
45	560	0.232
46	580	0.175
47	600	0.068
48	65	0.026

Table 16

Effect of Reagent concentration on the absorbance of Cobalt(II) and Isonitrosothiocamphor.

Concentration of Cobalt	:	50 ppm
Organic phase	:	10ml Chloroform
Time of equilibrium	:	1 min.
Wavelength	:	400 nm

Sr.No.	Volume of Isonitrosothiocamphor	Absorbance
1	0.1	0.640
2	0.2	0.660
3	0.3	0.681
4	0.4	0.685
5	0.5	0.690
6	0.6	0.690
7	0.7	0.691
8	0.8	0.691
9	0.9	0.691
10	1.0	0.691
11	1.5	0.691
12	2.0	0.691

Table 17

Absorbance of Cobalt (II) in chloroform with Isonitrosothiocamphor as function of time.

50 ppm of Cobalt (II) in 10 ml of chloroform at pH 7 equilibrated with respect to different time at 400nm.

Sr.No.	Time in minute	Absorbance
1	1	0.691
2	2	0.691
3	3	0.691
4	4	0.691
5	5	0.691
6	10	0.691
7	20	0.691
8	30	0.691
9	60	0.691
10	2hrs	0.691
11	12hrs	0.691
12	24hrs	0.691
13	48hrs	0.691
14	72hrs	0.691

Table 18

Absorbance of Cobalt (II) with the help of Isonitrosothiocamphor in chloroform at different pH

Concentration of Cobalt : 20 ppm

Organic phase : 10 ml Chloroform

Wavelength : 625 nm.

Sr.No	pH	Absorbance	% extraction
1	1.0	0.640	92.61 %
2	2.0	0.661	95.65 %
3	3.0	0.677	97.97 %
4	4.0	0.685	99.13 %
5	5.0	0.690	99.85 %
6	6.0	0.691	100.00 %
7	7.0	0.691	100.00 %
8	8.0	0.691	100.00 %
9	9.0	0.685	99.13 %
10	10.0	0.672	97.72 %

Table 19

Calibration Curve for Cobalt (II)

Organic phase : 10 ml chloroform
Time of equilibrium : 1 min.
Wavelength : 400 nm

Sr.No.	Conc. Of Cobalt in ppm	Absorbance
1	10	0.136
2	20	0.272
3	30	0.415
4	40	0.550
5	50	0.690
6	60	0.825
7	70	0.965
8	80	1.1

Table 20

Extraction of Cobalt (II) with Isonitrosothiocamphor using different solvent at pH 7

Organic phase : 10 ml

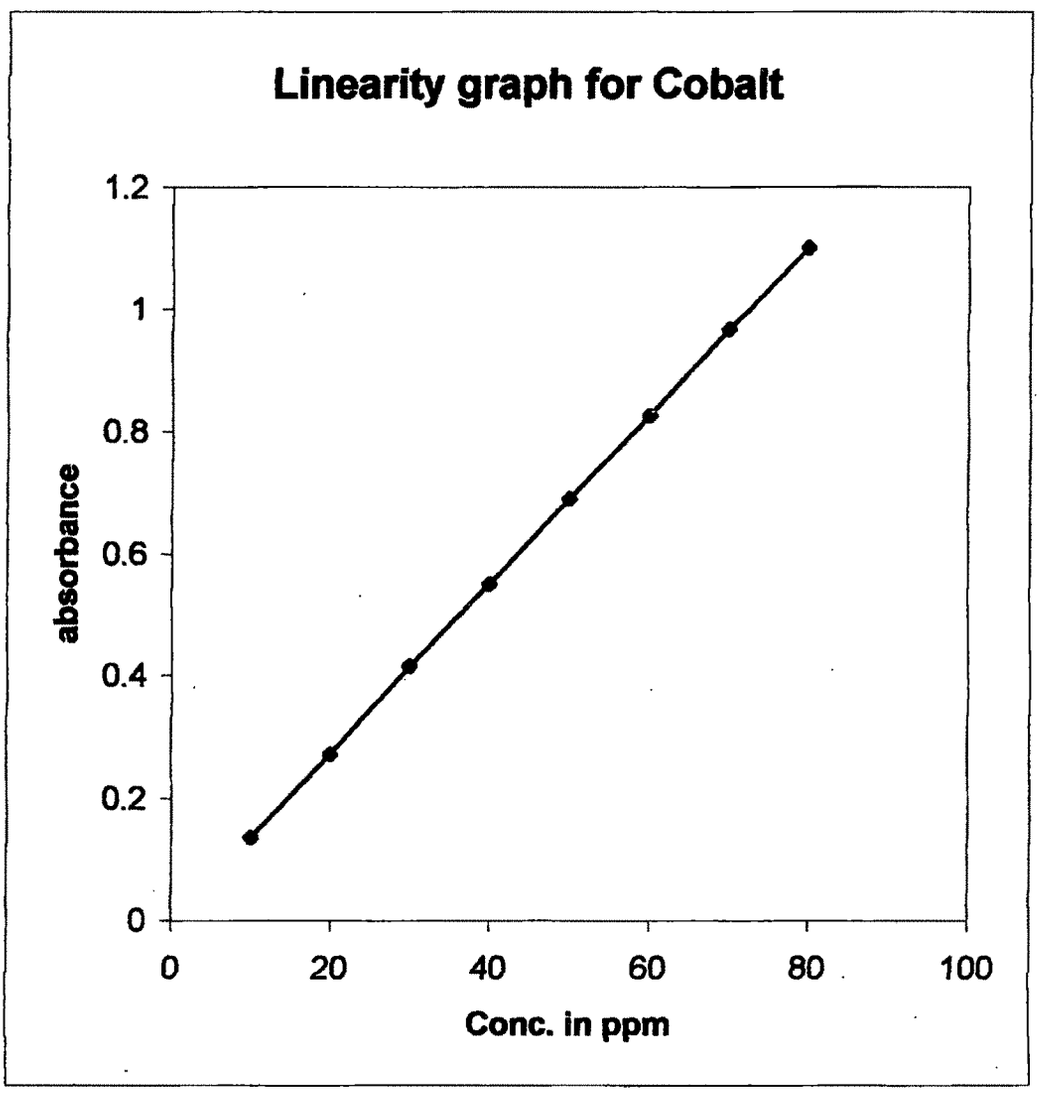
Time of equilibrium : 1 min.

Sr.No.	Solvent	Absorbance	% extraction
1	Chloroform	0.691	100.0%
2	Benzene	0.625	99.5%
3	Toluene	0.144	98.0%
4	Carbon tetra chloride	0.115	98.0%
5	Chlorobenzene	0.095	97.20%

Linearity graph for Cobalt

Calibration curve for cobalt at 400 nm in chloroform

Conc. of Cobalt in ppm	Absorbance
10	0.136
20	0.272
30	0.415
40	0.55
50	0.69
60	0.825
70	0.965
80	1.1



Infrared studies of Cobalt (II) Complex with isonitrosothiocamphor

For a long time, it was very difficult to make wavelength measurement in the infrared, Because of the lack of adequate detection means. The various functional group gives rise to certain absorption band in the infrared spectrum, to the extent that the occurrence of these bands necessary implies the existence of respective functional groups in the molecule.

A particular part of the infrared spectrum is referred to either by its wavelength or – and this is considered preferable, by its frequency. Wavelength is expressed simply the number of wave per centimeter and is equal to the reciprocal of the wavelength in centimeter.

It can happen that two or more solutions are equal to each other. In other words, two or more vibrations can have the same frequency. This vibration are called 'degenerate'. The degree of degeneracy is equal to the number of vibrations with equal frequency.

Diatomic molecule are the simplest possible system for theoretical studies of rotational & vibrational motion. They offer the possibility of compairing theoretical prediction with experimental results. For this reason diatomic molecules are usually treated separately in the theory of molecular spectroscopy.

The spectra of molecule in liquid or solid state, band varying in the width from narrow to broad, respectively the complexity of the transitions. The position, shape and intensity of these bands are the most important characteristics used in the spectroscopic studies of the organic molecules.

Functional groups determined with the help of infrared are as bellow.

1. **Nitroso compound** : N=O bond is stable in nitroso compounds is characterized by a stretching vibration in the range [15] 1621 -1488 cm^{-1}
Nitroso compound tend to dimerise, secondary primary nitroso compound readily rearrange to oxime. In monomeric state absorbs in the 1621-1488 cm^{-1} [16] region, but in the solution they exist preferably as dime rise and then absorbs near 1290 cm^{-1}

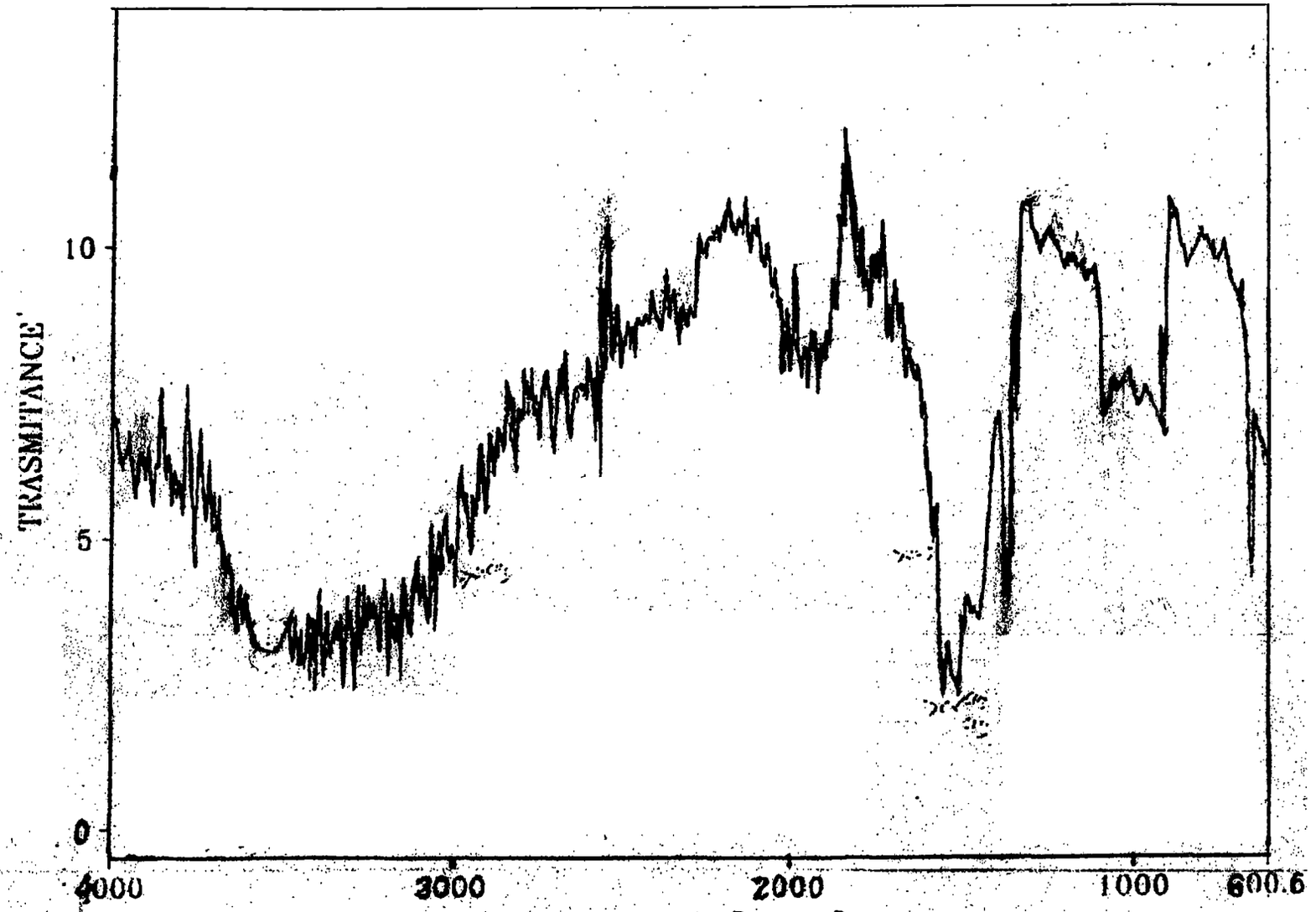
2. **→C– CH_3 group**: The mode of → C– CH_3 gives an observation at about [16] 2872 cm^{-1}

3. **>C=S group** : The range of >C=S group occurs in the range[17] of 1000-1400 cm^{-1}

4. **>C<** CH_3 **group** : The frequency of >C< CH_3 CH_3 is at about [18] 1340 -1460 cm^{-1}

Two new bands around 470 and 350 cm^{-1} appeared in the spectra of all the complexes, which could be assigned to complete vibrations having contribution from υ MN and υ MS.

υ – OH in free ligend disappear in the complex, and a new weak new band at 280 cm^{-1} appears. This indicates the deprotonation of the ligend molecule during the complexation. Further, the intensity of υ = C – decreases and it shifts to downward direction in the complex indicating thereby complaxation of oxygen side of the ligend.



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