

# Review on Spectrophotometric Method for Formation of Metal Complexes of Hydrazone Derivatives

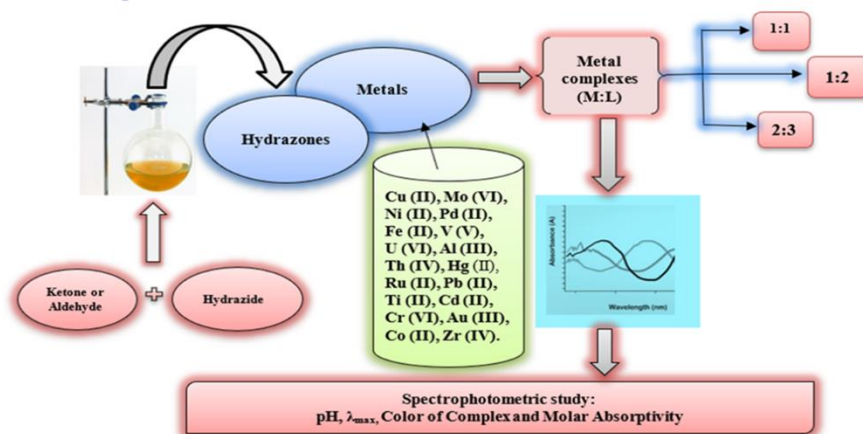
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## Abstract:

Hydrazone is a condensed compound of aldehyde or ketone with hydrazide. Hydrazones are very important organic analytical reagent and it is also used for spectrophotometric determination of the metal ion from real and simulated samples. Hydrazones forms various colored complexes with Copper (II) Molybdenum (VI), Nickel (II), Palladium (II), Iron (II), Vanadium (V), Uranium (VI), Aluminum (III), Thorium (IV), Mercury (II), Ruthenium (II), Lead (II), Titanium (II), Cadmium (II), Chromium (VI), Gold (III), Cobalt (II), Zirconium (IV) in 1:1, 1:2 and 2:3(metal: ligand) ratio. Metal complexes of hydrazones give  $\lambda_{\max}$  in range 300-590nm (under UV visible region) and at pH range 1-10.

## Graphical abstract:



## Key words:

Spectrophotometric method, Chromogenic reagents, Metal complexes, Hydrazone, Review

## Introduction

Hydrazone is a class of organic compounds with structure  $R_1R_2C=NNH_2$  and it is been formed by condensation of aldehyde or ketone with hydrazide. Complex forming agents like hydrazone derivatives [1-12] are becoming increasingly important in analytical chemistry such as gravimetric, titrimetric, colorimetric and spectrophotometric measurements [1]. Oximes and hydrazones are two different classes of chromogenic reagents widely used for the derivative spectrophotometric determination of metal ions [12]. Hydrazones are very important organic analytical reagent and it is also been used for spectrophotometric determination of the metal ion from real and simulated samples [13]. The metal complexes of hydrazones have diverse applications. Many researchers have synthesized these compounds as well as their metal complexes as plasticizers, polymerization inhibitors and antioxidants. They are used as fungicides and pesticides in biological and biochemical context. Metal ions in general and transition metals in particular are found to play an important role in industry, agriculture and plant nutrition, biological activities of living beings and medicines [17]. Hydrazones are reacted with many metal ions forming color complexes and act as chelating agents [19] and these compounds contain an azomethine nitrogen atom and responsible for their reactivity with number of transition metal ions which form colored complexes [20]. It has been widely used in pharmaceutical analysis, amino acid and protein analysis, clinical and environmental chemistry etc. but less often in inorganic analysis [20].

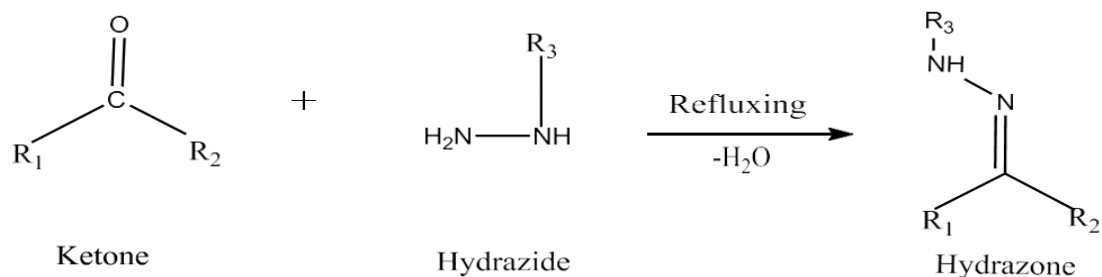
For the determination of metal ion at micro levels, there are several analytical techniques such as X-ray fluorescence spectroscopy, atomic absorption spectrophotometry, spectrofluorimetric and other techniques. Among UV-Visible spectrophotometric methods are mostly been used because they are cheaper, easy to handle and highly sensitive. Derivative Spectrophotometry (DS) is an analytical technique of great utility for extracting both qualitative and quantitative information from spectral curves composed of unresolved bands [18]. Derivative Spectrophotometry is a very useful approach for determining the concentration of single component in mixtures with overlapping spectra as it may eliminate interferences [17,20]. It is a very useful technique, in the sense that, it decreases the interference i.e., increase the tolerance limit value of the foreign ions. This method is found to be rapid, sensitive, selective, reproducible and free from interference of a large number of common metal ions [21]. The great interest towards derivative spectrophotometry is due to increased resolution of spectral bands, allowing the detection and location of the wavelengths of poorly resolved components of complex spectra and reducing the effect of spectral background interferences [22-24]. In general, the technique of solvent extraction is widely used in the spectrophotometric determination of metal ions. However, organic solvents such as benzene and chloroform are often carcinogenic, toxic and cause environmental pollution. It is significant to develop a method which does not involve solvent extraction [22-23].

Most of physically active hydrazones find application in the treatment of diseases like tuberculosis, leprosy, and mental disorders [25]. Hydrazones also act as herbicides, nematocides, rodenticides, plant growth regulators, antimicrobial [32], antituberculosis and

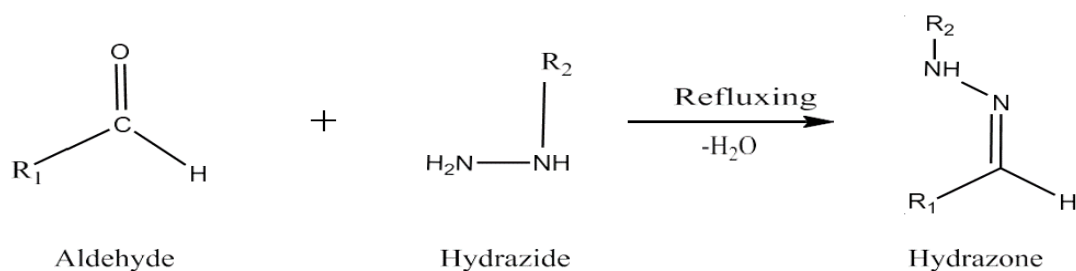
antitumor activities [30, 39]. Complex formation reactions are of great use in determining metal ions at the micro level or even Nano gram level. In this context organic reagents occupy a better place over inorganic reagents because of their complexing ability with metal ions of giving highly colored stable compounds [42, 59]. Benzoic hydrazones of carbonyl compounds have been used extensively for the spectrophotometric determination of metal ions in our laboratories [53]. Hydrazones can be synthesized in the laboratory by heating the appropriate substituted hydrazines or hydrazides with aldehydes and ketones [64] in various organic solvents like ethanol, methanol, tetrahydrofuran, butanol and sometimes with glacial acetic acid or ethanol-glacial acetic acid, Also hydrazones can be synthesized by the coupling of aryldiazonium salts with compounds containing active hydrogen.

## General reaction of synthesis of hydrazone

### Hydrazone from ketone [64]



### Hydrazone from aldehyde [64]



## Spectrophotometric determination of metal using hydrazine as a reagent

Spectrophotometric reagents are used for the determination of Copper(II) [1-14], Molybdenum(VI) [13-16], Nickel(II) [1,11,12,17,19], Palladium [21-28], Iron(II) [29-31], Vanadium(V) [32-35], Uranium(VI) [36-38], Aluminium(III) [31,39 41], Thorium(IV) [42,45], Mercury(II) [46,47], Ruthenium(II) [48,49], Lead(II) [50-52], Titanium(II) [53,54], Cadmium(II) [50,55,56], Chromium(VI) [50,57], Gold(III) [21,58,59], Cobalt(II) [60,61], Zirconium(IV) [62,63] and the established conditions like  $\lambda_{\text{max}}$ , pH, molar absorptivity and the metal-ligand composition are presented in Table 1-18.

**Table -1**  
**Various Reagents for Determination of Copper (II) by Spectrophotometric Methods**

Sr. no.	Reagent name	Metal ion	M: L	$\lambda_{\max}$ (nm)	Color of complex	pH	Molar Absorptivity in $L \text{ mol}^{-1} \text{ cm}^{-1}$	Ref. no.
1.	8-aceto-7-hydroxy coumarin hydrazone (AHCH)	Cu (II)	1:2	440	-	4.5	-	1
2.	2-(4-biphenyl) imidazo [1,2-] pyrimidine-3-hydrazone (BIPH)	Cu (II)	1:2	430	Yellowish green	4.0	$0.175 \times 10^4$	2
3.	2-Hydroxy-1-Naphthalene carboxaldehyde phenyl hydrazone (HNPH)	Cu (II)	1:2	360	Greenish yellow	9.2	$0.97 \times 10^4$	3
4.	2,3,4-trihydroxy Acetophenone phenyl hydrazone (THAPPH)	Cu (II)	1:2	385	Bluish green	2.5	$10.053 \times 10^4$	4
5.	2-acetylfuran benzoyl hydrazone (AFBH)	Cu (II)	1:1	360	Pale Greenish yellow	6.5	$2.05 \times 10^4$	5
6.	Salicylaldehyde acetoacetic acid hydrazone (SHZN)	Cu (II)	1:1	425	Greenish yellow	2.0	$22.5 \times 10^4$	6
7.	5-Chloro-2-hydroxy acetophenone phenyl hydrazone (CHAPH)	Cu (II)	1:2	380	Pale yellowish	7.0 to 8.0	$5.2 \times 10^4$	7
8.	5-Bromo-2-hydroxy acetophenone phenyl hydrazone (BHAPH)	Cu (II)	1:2	350	Pale yellowish	8.0 to 9.0	$2.5 \times 10^4$	7
9.	Salicylaldehyde benzoyl hydrazone (SAL-BH)	Cu (II)	1:1	404	Greenish yellow	2.27	$1.4 \times 10^4$	8
10.	3-methoxy salicylaldehyde-4-hydroxybenzoyl hydrazone (MSHBH)	Cu (II)	1:1	390	Yellow	5.0 to 6.0	$1.17 \times 10^4$	9
11.	Diacetylmonoxime-3-amino-4-hydroxybenzoyl hydrazone (DMAHBH)	Cu (II)	1:1	412	Bright yellow	8.0 to 10.0	$1.65 \times 10^4$	10

12.	Cinnamaldehyde-4-hydroxy benzoyl hydrazone (CMHBH)	Cu (II)	1:1	375	Yellow	9.0	$2.77 \times 10^4$	11
13.	4-hydroxy-3,5-dimethoxy benzaldehyde-4-hydroxy benzoyl hydrazone (HDMBHBH)	Cu (II)	1:1	348	Yellow	9.0	$3.41 \times 10^4$	11
14.	Diacetyl monoxime-4-hydroxy benzoyl hydrazone (DM-4-HBH)	Cu (II)	1:1	396	Yellowish green	10.5	$1.8 \times 10^4$	12

Copper is one of the most important metals after iron. It plays vital role in many fields either as metal or as salts such as industry, laboratory, medicine, food, and beverage [3]. Copper is an industrially valuable metal, it is used in preparation of coin, wire, medicine, alloys, fashioning metal products, transportation industry and thermal conductance [8]. Cu (II) forms stable complexes with a number of common organic reagents [1-12]. A huge number of organic reagents were reported for the spectrophotometric determination of the copper ion. Table-1 shows that copper (II) forms complex with some spectrophotometric reagents like AHCH [1], BIPH [2], HNPH [3], THAPPH [4], CHAPH [7] and BHAPH [7] in 1:2 (metal: ligand) ratio and with some other reagents like AFBH [5], SHZN [6], SAL-BH [8], MSHBH [9], DMAHBH [10], CMHBH [11], HDMBHBH [11] and DM-4-HBH [12] in 1:1 (metal: ligand) ratio. So, we can assume that ligands coordinate with metal ion in a monodentate and bidentate manner through the nitrogen atoms. These metal complexes show the maximum absorption in the range of 300 nm to 450 nm. HNPH, AFBH, CHAPH, BHAPH and DMAHBH in 10-fold and SHZN, MSHBH and DM-4-HBH in 5-fold molar excess of reagents are required for the intense color development of Cu (II). Spectrophotometric reagents BIPH and DM-4-HBH; HNPH, SHZN and SAL-BH; CHAPH and BHAPH; THAPPH; AFBH; MSHBH, CMHBH and HDMBHBH; DMAHBH give yellowish green; greenish yellow; pale yellowish; bluish green; pale greenish yellow; yellow; bright yellow color complexes in the pH range from 1.0 to 10.0. respectively [1-12]. Spectrophotometric reagent SHZN shows high molar absorptivity so it indicates that this reagent absorbs light well at 425 nm wavelength and BIPH shows low molar absorptivity at 430nm wavelength.

**Table-2**

**Various reagents for determination of Molybdenum (VI) by spectrophotometric methods**

Sr. no.	Reagent name	Metal ion	M:L	$\lambda_{\max}$ (nm)	Color of complex	pH	Molar Absorptivity in $L \text{ mol}^{-1} \text{ cm}^{-1}$	Ref. no.
1.	2,4-Dimethoxy benzaldehyde-4-hydroxy benzoyl	Mo (VI)	1:1	413	Yellow	3.5 to 4.5	$3.042 \times 10^4$	13

	hydrazone (DMBHBH)							
2.	5-Bromosalicylaldehyde isonicotinoyl hydrazone (5-BrSAINH)	Mo (VI)	1:1	390	Yellow	6.0	$2.0 \times 10^4$	14
3.	Salicylaldehyde acetoacetic acid hydrazone (SAAH)	Mo (VI)	1:2	470	Light yellowish	1.0	$16.00 \times 10^4$	15
4.	Diacetyl Monoxime Isonicotinoylhydrazone (DMIH)	Mo (VI)	1:1	346	Greenish Yellow	5.0	$1.93 \times 10^4$	16

A variety of reagents [13-16] were reported for the spectrophotometric determination of molybdenum (VI). Table-2 shows that molybdenum (VI) mostly forms yellow colored complex with Hydrazones [13-16] in acidic pH. The Salicylaldehyde acetoacetic acid hydrazone (SAAH) reagent shows high molar absorptivity at 470 nm wavelength. The spectrophotometric reagents [13-16] shows maximum absorption under range 390 nm to 500 nm. Table-2 is revealing that DMBHBH, 5-BrSAINH and DMIH form complex in 1:1 (M:L) and SAAH forms complex in 1:2 (M: L) molar ratio with Mo (VI).

**Table-3**  
**Various reagents for determination of Nickel (II) by spectrophotometric methods**

Sr. no.	Reagent name	Metal Ion	M:L	$\lambda_{\max}$ (nm)	Color of complex	pH	Molar Absorptivity in $L \text{ mol}^{-1} \text{ cm}^{-1}$	Ref. No.
1.	2,4-Dimethoxy benzaldehyde Isonicotinoyl hydrazone (DMBIH)	Ni (II)	1:1	410	Yellow	9.0	$5.92 \times 10^4$	17
2.	8-aceto-7-hydroxy coumarin hydrazone (AHCH)	Ni (II)	1:2	570	-	5.5	-	1
3.	5-Bromo-2-hydroxy-3-methoxy benzaldehyde-p-hydroxybenzoic hydrazone(5-BHMBHBH)	Ni (II)	-	440	Green	4.0 to 8.0	-	18
4.	3-methoxy salicylaldehyde-4-hydroxybenzoyl hydrazone (MSHBH)	Ni (II)	1:1	425	Yellow	5.0 to 6.5	$1.27 \times 10^4$	19

5.	3,5-Dimethoxy-4-hydroxybenzaldehyde isonicotinylohydrazone (DMHBIH)	Ni (II)	1:1	386	Bright yellow	8.5 to 9.5	$1.22 \times 10^4$	20
6.	4-hydroxy-3,5-dimethoxy benzaldehyde-4-hydroxy benzoyl hydrazone (HDMBHBH)	Ni (II)	1:1	408	Yellow	9.0	$3.22 \times 10^4$	11
7.	Diacetyl monoxime-4-hydroxy benzoyl hydrazone (DM-4-HBH)	Ni (II)	1:1	380	Light green	9.0	$2.0 \times 10^4$	12
8.	Cinnamaldehyde-4-hydroxy benzoyl hydrazone (CMHBH)	Ni (II)	1:1	400	Yellow	9.0	$2.17 \times 10^4$	11

From the table-3, it can be concluded that DMBIH [17], AHCH [1], 5-BHMBHBH [18], MSHBH [19], DMHBIH [20], HDMBHBH, CMHBH [11] and DM-4-HBH [12] are potential reagent for the spectrophotometric determination of Ni (II) in pH range of 4.0 to 9.0. Nickel shows yellow color complexes with DMBIH, MSHBH, HDMBHBH and CMHBH reagents, green color complexes with BHMBHBH and DM-4-HBH reagents and bright yellow color complexes with DMHBIH reagent. These complexes have maximum absorption in 380 nm to 570 nm range. At 410 nm wavelength the reagent 2, 4-Dimethoxy benzaldehyde isonicotinylohydrazone (DMBIH) shows highest molar absorptivity. Above reagents form complex with Ni (II) in 1:1 (M:L) molar ratio except AHCH [1]. Nickel complex of AHCH shows 1:2 (M:L) ratio.

**Table-4**  
**Various reagents for determination of Palladium (II) by spectrophotometric methods**

Sr. no.	Reagent name	Metal Ion	M:L	$\lambda_{\max}$ (nm)	Color of complex	pH	Molar Absorptivity in $L \text{ mol}^{-1} \text{ cm}^{-1}$	Ref. No.
1.	2,4-Dihydroxyl acetophenone-p-hydroxylbenzoylhydrazone (RPPHBH)	Pd (II)	1:1	375	Pale Green 15-fold	5.5	$0.42 \times 10^4$	21
2.	Cinnamaldehydeisonicotinylohydrazone (CINH)	Pd (II)	1:1	412	Yellow 10-fold	3.0 to 6.0	$1.03 \times 10^4$	22
3.	3,5-Dimethoxy-4-hydroxybenzaldehyde isonicotinylohydrazone (DMHBIH)	Pd (II)	1:1	382	Bright yellow 5-fold	5.5	$2.44 \times 10^4$	23

4.	3-methoxy salcinaldehyde-4-hydroxybenzoyl hydrazone (MSHBH)	Pd (II)	1:1	412	Orange yellow 5-fold	4.5	$1.03 \times 10^4$	24
5.	3,4-Dihydroxy benzaldehydeisonicotinoyl hydrazone [3,4-DHBINH]	Pd (II)	1:1	380	Yellow 10-fold	3.0	$0.53 \times 10^4$	25
6.	Isonitroso p-methyl acetophenone phenyl hydrazone (HIMAPH)	Pd (II)	1:2	470	Yellow	0.0 to 5.0	$1.3305 \times 10^4$	26
7.	2-hydroxy-1-naphthaldehyde-p-hydroxybenzoic hydrazone (HNHBH)	Pd (II)	1:1	430	Greenish yellow	4.0	$2.48 \times 10^4$	27
8.	2-hydroxy-5-methylacetophenone Isonicotinoyl hydrazone (HMAINH)	Pd (II)	1:1	385	Yellow	Acidic medium	$0.5320 \times 10^4$	28

Palladium has strong affinity for nitrogen containing ligands. It is used in the manufacture of watch bearings, springs, balance wheels, air craft spark plugs, blood sugar test strips and also for mirrors in scientific instruments [23]. Its alloys are used in manufacture of jewelry, dental and medicinal devices [25]. From Table-4, the reagents such as RPPHBH [21], CINH [22], DMHBIH [23], MSHBH [24], DHBINH [25], HIMAPH [26], HNHBH [27] and APH [28] are used as chromogenic reagent for determination of Pd (II). Palladium (II) forms pale green color complex with RPPHBH, yellow color with CINH, 3,4-DHBINH, HIMAPH and HMAINH, bright yellow with DMHBIH, orange yellow color with MSHBH, greenish yellow color with HNHBH at particular pH range and gives maximum absorption in 380 nm to 470 nm range. In above all reagents 3, 5-Dimethoxy-4-hydroxybenzaldehyde isonicotinoyl hydrazone (DMHBIH) shows highest molar absorptivity at 382 nm wavelength and 2, 4-Dihydroxyl acetophenone-p-hydroxylbenzoylhydrazone (RPPHBH) shows lowest molar absorptivity at 375 nm wavelengths. RPPHBH, CINH, DMHBIH, MSHBH, 3, 4-DHBINH, HNHBH and HMAINH forms complex in 1:1 (M:L) and HIMAPH in 1:2 (M:L) stoichiometry. A 15-fold molar excess of RPPHBH, 10-fold molar excess of CINH and 3, 4-DHBINH and 5-fold molar excess of DMHBIH and MSHBH are adequate for intense color development with palladium (II).

**Table-5**

**Various reagents for determination of Iron (II) by spectrophotometric methods**

Sr. no.	Reagent name	Metal Ion	M:L	$\lambda_{\max}$ (nm)	Color of complex	pH	Molar Absorptivity in $L \text{ mol}^{-1} \text{ cm}^{-1}$	Ref. No.
1.	2-hydroxy-1-naphthalaene carboxaldehyde phenyl hydrazone (HNPH)	Fe (III)	1:3	510	Red	6.0	$0.31 \times 10^4$	29



2.	Diacetyl monoxime isonicotonylhydrazone (DMIH)	Fe (III)	1:1	355	Yellow	9.0	$3.83 \times 10^4$	30
3.	5-Bromo-2-hydroxy benzaldehyde-4-hydroxy benzoic hydrazone (5-BHMBHBH)	Fe (III)	-	480	Brown	4.0	$3.233 \pm 0.004 \times 10^4$	31

Iron is broadly used in production of all the metals [29, 30]. Iron is an important part of hemoglobin, and it is working as the red coloring agent of the blood in human bodies for transportation of oxygen. It is also an essential element in plant enzymes, peroxidase, catalase and cytochrome oxidase [30]. From the table-5, Fe (III) forms red colored complex with HNPH [29] at 1:3 (M:L) ratio. Color of Fe (III) complex with DMIH [30] and 5-BHMBHBH [31] are yellow and brown respectively. The Fe (III) complexes show maximum absorption in the range of 355 nm to 510 nm in pH range 4.0 to 9.0.

**Table-6**  
**Various reagents for determination of Vanadium (V) by spectrophotometric methods**

Sr. no.	Reagent name	Metal Ion	M:L	$\lambda_{\max}$ (nm)	Color of complex	pH	Molar Absorptivity in $L \text{ mol}^{-1} \text{ cm}^{-1}$	Ref. No.
1.	2-methyl-8-quinolinol (MQ)	V (V)	1:2	400	Light brown	-	$0.244 \times 10^4$	32
2.	Salicylaldehyde acetoacetic acid hydrazone (SAAH)	V (V)	1:2	460	Light yellow	2.0	$2.2 \times 10^4$	33
3.	Diacetyl monoxime salicyloyl hydrazone (DMSH)	V (V)	1:1	405	Yellow	-	$1.30 \times 10^4$	34
4.	2,3,4-trihydroxy acetophenone phenyl hydrazone (THAPPH)	V (V)	1:2	390	Pale yellow 5-fold	2.8	$19.99 \times 10^4$	35

Analyzing table-6, V (V) forms yellow colored complex with spectrophotometric reagents such as SAAH [33], DMSH [34], THAPPH [35]. DMSH forms complex with Vanadium in 1:1 molar ratio while MQ, SAAH, THAPPH form complex with Vanadium in 1:2 (M:L) molar ratio. V (V) complexes show maximum absorption in the range 390 nm to 460 nm in the pH range 2.0 to 3.0. Vanadium complex of THAPPH shows high molar absorptivity with compare to other vanadium complex.

**Table-7**  
**Various reagents for determination of Uranium (VI) by spectrophotometric methods**

Sr. no.	Reagent name	Metal Ion	M:L	$\lambda_{\max}$ (nm)	Color of complex	pH	Molar Absorptivity in $L \text{ mol}^{-1} \text{ cm}^{-1}$	Ref. No.
1.	2-hydroxy-3-methoxy benzaldehyde isonicotinylohydrazone (HMBIH)	U(VI)	1:1	374	Yellow 5-fold	4.0	$1.05 \times 10^4$	36
2.	5-Bromosalicylaldehyde isonicotinylohydrazone (5-BrSAINH)	U(VI)	1:1	395	Pale Yellow 25-fold	5.0	$1.17 \times 10^4$	37
3.	Diacetyl monoxime isonicotinylohydrazone (DMIH)	U(VI)	1:1	364	Yellow 5-fold	3.2 to 5	$1.63 \times 10^4$	38

Table 7 indicates that HMBIH [36], 5-BrSAINH [37] and DMIH [38] form complexes with Uranium in 1:1(M:L) ratio. Uranium complexes show maximum absorption in the range of 364 nm to 395 nm. The molar absorptivity value of the U (VI) is in the range of  $1.05 \times 10^4$  to  $1.63 \times 10^4 L \text{ mol}^{-1} \text{ cm}^{-1}$ . Uranium forms yellow color complex with HMBIH, DMIH and pale-yellow color complex with 5-BrSAINH in acidic pH. A 5-fold of molar excess of HMBIH, DMIH and 25-fold of molar excess of 5-BrSAINH is required for intense color development of Uranium.

**Table-8**  
**Various reagents for determination of Aluminum (III) by spectrophotometric methods**

Sr, no	Reagent name	Metal Ion	M:L	$\lambda_{\max}$ (nm)	Color of complex	pH	Molar Absorptivity in $L \text{ mol}^{-1} \text{ cm}^{-1}$	Ref. No.
1.	5-Bromo-2-hydroxy benzaldehyde-4-hydroxy benzoic hydrazone (5-BHMBHBH)	Al (III)	-	390	Yellow	4.0	$2.66 \pm 0.004 \times 10^4$	31
2.	Diacetyl monoxime isonicotinylohydrazone (DMIH)	Al (III)	1:1	355	Greenish yellow 5-fold	8.0	$2.69 \times 10^4$	39
3.	2-Hydroxy-3-methoxybenzaldehyde-p-	Al (III)	2:3	410	Yellow 15-fold	4.5 to 5.5	$4.19 \times 10^4$	40

	hydroxybenzoichydrazo ne (HMBAHBH)							
4.	2-Hydroxy naphthaldehyde benzoyl hydrazone (HNPBH)	Al (III)	2:3	412	-	5.0	$2.21 \times 10^4$	41

Table-8 shows that Aluminum (III) form complexes in 2:3 (M:L) ratio with HMBAHBH, HNPBH and 1:1 (M:L) ratio with DMIH. Aluminum complexes show maximum absorption in the range of 355 nm to 412 nm. Above Al (III) complexes show molar absorptivity in the range of  $2.21 \times 10^4$  to  $4.19 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ . It reveals that reagents were more sensitive for metal ions. Aluminum forms yellow colored complex with 5-BHMBHBH, HNPBH and greenish yellow colored complex with DMIH in the pH range 4.0 to 8.0. A 5-fold and 15-fold molar excess of DMIH, HMBAHBH is required for deep color development of Aluminum, respectively.

**Table-9**  
**Various reagents for determination of Thorium (IV) by spectrophotometric methods**

Sr. no.	Reagent name	Metal Ion	M:L	$\lambda_{\text{max}}$ (nm)	Color of complex	pH	Molar Absorptivity in $\text{L mol}^{-1} \text{ cm}^{-1}$	Ref. No.
1.	Diacetyl monoxime isonicotinoyl hydrazone (DMIH)	Th(IV)	1:1	352	Yellow 5-fold	5.0	$2.265 \times 10^4$	42
2.	3,5-Dimethoxy-4-hydroxybenzaldehyde isonicotinoylhydrazone (DMHBIH)	Th (IV)	1:1	390	Yellow 10-fold	3.0	$4.84 \times 10^4$	43
3.	2,3,4-trihydroxy acetophenone phenyl hydrazone (THAPPH)	Th(IV)	1:1	390	Yellow	3.0	$32.46 \times 10^4$	44
4.	5-Bromo-2-hydroxy-3-methoxy benzaldehyde-4-hydroxy benzoic hydrazone (5-BHMBHBH)	Th (IV)	1:1	400	Yellow 5-fold	2.0	$0.8766 \times 10^4$	45

Thorium is a naturally occurring white metal. It is contaminated with the oxide. Thorium slowly tarnishes in air, becomes grey and eventually black. Thorium is found in small amounts in most rocks and soils [42-44]. DMIH, DMHBIH, THAPPH and 5-BHMBHBH give yellow colored complex with Thorium in the pH range of 2.0. to 5.0. Above reagents form complexes with Th (IV) in 1:1 (M:L) stoichiometry. Maximum absorptions are in the range from 352 nm to 400 nm. A 5-fold of molar excess of DMIH and 5-BHMBHBH and 10-fold of molar excess of DMHBIH are required for the deep color development of the Thorium. THAPPH complex

shows highest molar absorptivity and 5-BHMBHBH complex shows lowest molar absorptivity.

**Table-10**  
**Various reagents for determination of Mercury (II) by spectrophotometric methods**

Sr, no	Reagent name	Metal ion	M:L	$\lambda_{\max}$ (nm)	Color of complex	pH	Molar Absorptivity in $L \text{ mol}^{-1} \text{ cm}^{-1}$	Re f. No.
1.	Alpha amyln cinnamaldehyde isonicotionoylhydrazone (ACINH)	Hg (II)	1:1	391	Yellow 10-fold	10.0	$2.78 \times 10^4$	46
2.	Isonitroso p-isopropyl acetophenone phenyl hydrazone (HIPAPH)	Hg (II)	1:2	395	Light yellow 25-fold	7.0 to 10.0	$2.678 \times 10^4$	47

Mercury is the injurious environmental pollutant. Due to its harmful nature; in water sample the determination of Hg (II) in a micro amount has great importance [46]. ACINH and HIPAPH gives yellow and light-yellow colored complex with Mercury, respectively in pH range 7.0 to 10.0. Mercury forms 1:2 (M:L) complex with reagent HIPAPH and this complex shows maximum absorption at 395 nm. A 25-fold of molar excess of HIPAPH and 10-fold of molar excess of ACINH is required for the development of maximum color intensity of Hg (II). ACINH and HIPAPH complexes show almost equal molar absorptivity.

**Table-11**  
**Various reagents for determination of Ruthenium (III) by spectrophotometric methods**

Sr. no.	Reagent name	Metal ion	M:L	$\lambda_{\max}$ (nm)	Color of complex	pH	Molar Absorptivity in $L \text{ mol}^{-1} \text{ cm}^{-1}$	Ref. No.
1.	3,5-dimethoxy-4-hydroxybenzaldehyde isonicotionoyl hydrazone (DMHBIH)	Ru (III)	1:1	390	Brownish yellow 10-fold	4.2 to 5	$1.7 \times 10^4$	[48]
2.	Diacetyl monoxime isonicotionoyl hydrazone (DMIH)	Ru (III)		346	Purple	4.5	$1.4 \times 10^4$	[49]

Generally, Ruthenium complexes show higher resistance to hydrolysis and have extra selective action on tumors. It is a versatile catalyst and newly ruthenium complexes have been used in the detection of proteins and chlorpheniramine and investigated as anticancer drugs. Ruthenium plays not biological role but does strongly stain human skin, may be carcinogenic and bio- accumulates in bone [48]. Ruthenium forms a brownish yellow and purple colored

complex with DMHBIH and DMIH at pH 4.25 and 4.5 respectively. DMHBIH forms complex with Ruthenium in 1:1 (M:L) ratio. Molar absorptivity of DMHBIH complex is  $1.7 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$  and DMIH complex is  $1.4 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ . Maximum absorption of DMHBIH and DMIH are 390 nm and 346 nm respectively.

**Table-12****Various reagents for determination of Lead (II) by spectrophotometric methods**

Sr. no.	Reagent Name	Metal ion	M:L	$\lambda_{\text{max}}$ (nm)	Color of complex	pH	Molar Absorptivity in $\text{L mol}^{-1} \text{ cm}^{-1}$	Ref. No.
1	Glutaraldehyde phenyl hydrazone (GPH)	Pb (II)	2:1	395	-	6.5 to 7.5	$2.213 \times 10^4$	50
2.	4-hydroxy-3,5-dimethoxy benzaldehyde-4-hydroxy benzoyl hydrazone (HDMBHBH)	Pb (II)	1:1	386	Yellow 10-fold	10.0	$2.66 \times 10^4$	51
3.	Cinnamaldehyde 4-hydroxy benzoyl hydrazone (CMHBH)	Pb (II)	1:1	430	Yellow	9.0	$3.47 \times 10^4$	52

Lead compounds are very toxic for animals [51]. It is easily get deposited in blood, kidney, and reproductive system, nervous system, brain, and intense lead can give toxic results like colic shock, severe anemia and irreversible brain damage. [52]. Lead forms yellow colored complex with HDMBHBH and CMHBH at basic pH. The stoichiometric composition of Pb complexes is 1:1 (M:L) with HDMBHBH and CMHBH and 2:1(M:L) with GPH. Molar absorptivity of Pb complexes ranges in between  $2.213 \times 10^4$  to  $3.47 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ . A 10-fold of molar excess of HDMBHBH reagent is necessary to obtained maximum color intensity of palladium.

**Table-13****Various reagents for determination of Titanium (IV) by spectrophotometric methods**

Sr. no.	Reagent name	Met al ion	M:L	$\lambda_{\text{max}}$ (nm)	Color of complex	pH	Molar Absorptivity in $\text{L mol}^{-1} \text{ cm}^{-1}$	Ref. No.
1.	2-hydroxy-1-naphthaldehyde-p-hydroxy benzoic hydrazone (2-HNHBH)	Ti (IV)	1:1	405	Orange brown 10-fold	2.0	$1.68 \times 10^4$	53
2.	3,4-Dihydroxy benzaldehyde isonicotioylhydrazone (3,4-DHBINH)	Ti (IV)	1:2	370	Yellow	3.5	$1.489 \times 10^4$	54

Titanium compounds are deeply corrosive resistant to chloride solution as well as sea water, nitric acid, chlorine dioxide, Sulphur dioxide and other bleaching agents. Titanium is used as an alloy [53]. Metallic titanium is a strong like steel, but much lighter, yet it is heavier than aluminum and twice as strong [54]. Rare numbers of hydrazones are available for the spectrophotometric determination of titanium (IV) [53, 54]. 2-HNHBH shows maximum absorption at 405 nm and 3,4-DHBINH shows maximum absorption at 370 nm. Orange brown and yellow colored complex is formed with Ti (IV) by 2-HNHBH and 3,4-DHBINH respectively in acidic medium. 2-HNHBH forms complex in 1:1 (M:L) ratio and 3,4-DHBINH form it with 1:2 (M:L) ratio. 2-HNHBH and 3,4-DHBINH show molar absorptivity which are  $1.68 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$  and  $1.489 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$  respectively. The findings of its pH, maximum absorbance, molar absorptivity and stoichiometry are the source for determining the potential utility of 2-HNHBH and 3,4-DHBINH as a chromogenic reagent for titanium (IV).

**Table-14**  
**Various reagents for determination of Cadmium (II) by spectrophotometric methods**

Sr, no	Reagent name	Metal Ion	M:L	$\lambda_{\text{max}}$ (nm)	Color of complex	pH	Molar Absorptivity in $\text{L mol}^{-1} \text{ cm}^{-1}$	Ref. No.
1.	Diacetyl monoxime-3-amino-4-hydroxy benzoyl hydrazone (DMAHBH)	Cd (II)	1:1	378	Yellow 10-fold	8.0 to 9.0	$2.94 \times 10^4$	55
2.	Glutaraldehyde phenyl hydrazone (GPH)	Cd (II)	2:1	387	-	6.5 to 7.5	$2.213 \times 10^4$ to $2.460 \times 10^4$	50
3.	Cinnamaldehyde-4-hydroxy benzoyl hydrazone (CMHBH)	Cd (II)	1:1	383	Yellow 10-fold	8.0 to 9.0	$5.6 \times 10^4$	56

Cadmium occurs in association with zinc in minerals. Growing plants acquire and concentrate Cd (II) within the same biochemical setup. It is a lustrous, silver-white, ductile and highly pliable metal. It is not soluble in alkalis but soluble in acids [55]. A few numbers of hydrazones are available for the spectrophotometric determination of cadmium [55-56]. Reagents like DMAHBH, GPH and CMHBH which are used as a chromogenic reagent. Above cadmium complexes gives yellow color and a 10-fold molar excess of reagent is required for intense color development of Cd (II). The maximum absorption of this reagent is in 378 nm to 383 nm range. CMHBH gives highest molar absorptivity therefore it can conclude that it absorbs higher amount of light and exhibit more sensitivity than other reagents.

**Table-15**  
**Various reagents for determination of chromium (VI) by spectrophotometric methods**

Sr. no.	Reagent name	Metal ion	M:L	$\lambda_{\max}$ (nm)	Color of complex	pH	Molar Absorptivity in $L \text{ mol}^{-1} \text{ cm}^{-1}$	Ref. No.
1.	Glutaraldehyde phenyl hydrazone (GPH)	Cr (VI)	2:1	360	-	6.5 to 7.5	$2.213 \times 10^4$ to $2.460 \times 10^4$	50
2.	3,4-Dihydroxy benzaldehyde isonicotinyol hydrazone (3,4-DHBINH)	Cr (VI)	1:1	400	Yellow	5.5	$1.35 \times 10^4$	57

Cr (III) and Cr (VI) are two stable oxidation states of chromium in natural water. In which Cr (III) is considered to be necessary to mammals for the upkeep of glucose, lipid and protein metabolism, whereas Cr (VI) is a toxic and carcinogenic form [57]. The toxicity of Cr (VI) compounds derives from its ability to diffuse through cell membrane and oxidize biological molecules [57]. The Cr (VI) gives a yellow-colored complex with 3,4-DHBINH in acetate buffer of pH 5.5 and forms 1:1(M:L) complex and GPH forms 2:1(M:L) complex with Cr (VI). GPH and 3,4-DHBINH have maximum absorbance at 360 and 400 nm.

**Table-16**  
**Various reagents for determination of Gold (III) by spectrophotometric methods**

Sr. no.	Reagent name	Metal Ion	M:L	$\lambda_{\max}$ (nm)	Color of complex	pH	Molar Absorptivity in $L \text{ mol}^{-1} \text{ cm}^{-1}$	Ref. No.
1.	2,4-Dihydroxy acetophenone-p-hydroxy benzoyl hydrazone (RPPHBH)	Au (III)	1:1	590	Violet 10-fold	5.5	$0.5 \times 10^4$	21
2.	3,5-Dimethoxy-4-hydroxy benzaldehyde benzoyl hydrazone (DMBBH)	Au (III)	1:2	380	Wine red 10-fold	5.0	$2.32 \times 10^4$	58
3.	Diacetyl monoxime isonicotinyol hydrazone (DMIH)	Au (III)	1:1	361	Yellow	4.5	$1.50 \times 10^4$	59

Some hydrazone reagents [21, 58, 59] are used for the spectrophotometric determination of Au (III). There are not many methods reported for the spectrophotometric determination of gold (III) especially using hydrazones. Most of the spectrophotometric methods proposed for the

determination of gold (III) in ternary system or surfactant effects or oxidizing agents [59]. Au (III) gives violet colored complex with RPPHBH, wine-red colored complex with DMBBH, yellow colored complex with DMIH with 1:1 (M:L) and 1:2 (M:L) at acidic pH. Gold complexes show maximum absorption in range of 361 nm to 590 nm. A10-fold molar excess of RPPHBH and DMBBH is required for the intense color development of gold. DMBBH exhibits highest molar absorptivity.

**Table-17**  
**Various reagents for determination of Cobalt (II) by spectrophotometric methods**

Sr. no.	Reagent name	Metal Ion	M:L	$\lambda_{\max}$ (nm)	Color of complex	pH	Molar Absorptivity in $L \text{ mol}^{-1} \text{ cm}^{-1}$	Ref. No.
1.	3,4-Dihydroxy benzaldehyde-1-(3-chloro-2-quinoxaliny) hydrazone (DHBCQH)	Co (II)	1:2	450	-	4.0 to 6.0	$44.5 \times 10^4$	60
2.	4-Hydroxy 3,5-dimethoxy benzaldehyde-4-hydroxy benzoyl hydrazone (HDMBHBH)	Co (II)	1:1	397	Light Green 10-fold	9.0	$4.37 \times 10^4$	61
3.	Cinnamaldehyde-4-hydroxy benzoyl hydrazone (CMHBH)	Co (II)	1:2	393	Light yellow 10-fold	9.0	$6.5 \times 10^4$	61

Cobalt is found generally in the form of ores. Cobalt act as an important role in the nitrogen fixation by bacteria and also an integral part of vitamin-B<sub>12</sub>. Mammals require small amount of Cobalt salts [61]. For the determination of Cobalt (II), at microgram amounts, a number of hydrazone derivatives and more than a few analytical techniques such as AAS, ICP-AES, ICP, X-Ray fluorescence spectroscopy and UV-visible spectrophotometry can be employed. Among them, spectrophotometric methods are chosen because they are cheaper and easy to handle [61]. DHMBHBH and CMHBH give light green and light-yellow colored complex with Co (II) respectively during pH range of 4 to 9. A 10-fold molar excess of reagents are required for the deep color development of cobalt. These complexes show maximum absorbance in the range 393 to 450 nm. DHMBHBH forms 1:1 (M:L) and DHBCQH and CMHBH form 1:2 (M:L) composition with cobalt. DHBCQH has the highest molar absorptivity at 450 nm.



**Table-18**  
**Various reagents for determination of Zirconium (IV) by spectrophotometric methods**

Sr. no.	Reagent name	Metal Ion	M:L	$\lambda_{\max}$ (nm)	Color of complex	pH	Molar Absorptivity in $L \text{ mol}^{-1} \text{ cm}^{-1}$	Ref. No.
1.	Diacetyl monoxime salicyloyl hydrazone (DMSH)	Zr (IV)	1:2	380	Yellow	Acidic medium	$1.82 \times 10^4$	62
2.	2,4-Dimethoxy benzaldehyde isonicotinoylhydrazine (2,4-DMBINH)	Zr (IV)	1:1	391	Yellow	8.0	-	63

Zirconium is used in the ceramic industry to produce enamels and in the production of copper and its alloys and in the production of optical eyeglasses with high refractive index [62]. Table-18 indicates that the reagents DMSH and 2,4-DMBINH give yellow color complex with zirconium in varied range of pH. The stoichiometric composition of the metal complexes are 1:1(M:L) and 1:2(M:L) for 2,4-DMBINH and DMSH respectively. The maximum absorption of DMSH complex is at 380 nm and of 2,4-DMBINH complex is at 391 nm.

## Conclusion

Based on the above review the trace amounts of transition metal and inner transition metals can be determined by spectrophotometric methods. Hydrazones are extensively used for the spectrophotometric determination of metal ions. Based on the above tables-1 to 18 it can be said that all metal complexes are mostly gives  $\lambda_{\max}$  in range 300-590nm (under UV visible region) and at pH range 1-10. Above all hydrazone metal complexes prepared in 1:1, 1:2(metal: ligand) ratio, and some complexes are 2:3(metal: ligand) ratio. These measurements indicated that the ligands coordinate with the metal ion in a monodentate, bidentate and tridentate manner through the nitrogen atoms. The hydrazones are precious reagent and the U.V. spectrophotometric method is simpler, accurate and effective alternative for the determination of metal ion in various real and simulated sample.

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