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A Comprehensive Review on Analytical Applications of Hydrazone Derivatives

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Abstract: This review covers a summary of analytical applications of hydrazone derivatives in a systematic manner (1961-2021), which will help researchers in the design and development of hydrazone derivatives as potential candidates in medicinal, pharmaceutical, catalytic, and analytical chemistry, especially in the separation, identification, and detection of several metal ions, anions, organic molecules, and water in various real and synthetic samples. In addition to these, hydrazone derivatives may be used as light emitting diodes, for synthesis of DSSC, nanoparticles and polymers, as corrosion inhibitors, as dyes, etc. This review does not include all papers in this field, but it does synthesize all significant works on the subject.

Keywords: Hydrazone, analytical applications, DSSC, detection of metals, non-linear optical devices

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INTRODUCTION

Hydrazones are a class of azomethine with a -C=N-N- linkage, prepared by the reaction of hydrazide and aldehydes or ketones (1). In hydrazones, azomethine group gained much importance as compared to other organic compounds because carbon has both electrophilic and nucleophilic nature while both nitrogen atoms are in nucleophilic nature (2,3). All the hydrazone derivatives exist in *keto-enol* tautomerism via intermolecular proton transfer (4) and cis-trans form depends on azomethine bond, solvent, pH, and concentration. Hydrazone derivatives are considered as both proton donor and proton acceptor species and show intermolecular and intermolecular hydrogen bonding (5). This unique characteristic of hydrazone derivatives makes a them very important class of compounds.

In the past few decades, hydrazone and their derivatives possessed many biological applications (6) (Figure 1,2) like antifungal ((E)-N'-[(5-Methyl-7-nitrobenzofuran-2-yl)methylene]-benzo-hydrazide, ***1***) (7), antibacterial (2,3,4 pentanetrione-3-[4-[[(5-nitro-2-furyl)methylene]-hydrazino]-carbonyl]phenyl]-hydrazone, ***2***) (8), intestinal antiseptic (4-hydroxybenzoic acid[(5-nitro-2-furyl)-methylene]-hydrazide, ***3***) (9), anticonvulsant (N'-(4-chloro-benzylidene)-nicotinohydrazide, ***4***) (10), analgesic (Decanoic acid (4-methoxy benzylidene)hydrazide, ***5***) (11), anti-cancer (1H-pyrazole-5-carbohydrazide hydrazone, ***6***) (12), anti-inflammatory (Salicylaldehyde-2-(4-isobutyl-phenyl)-propionyl hydrazone, ***7***) (13), anti-platelet *(*Indole-3-carboxaldehyde 4-methoxyphenyl-hydrazone*,* ***8***) (14), anti-viral (N'-benzylidene-2-((4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-amino)acetohydrazide, ***9***) (15), anti-proliferative (2-(2-(2,4,6-trioxotetrahydro-pyrimidin-5(2H)-ylidene) hydrazinyl) benzoic acid, ***10)*** (16), anti-malarial (4-((2-(benzo[d]thiazol-2-yl)hydrazineylidene)-methyl)benzene-1,2-diol, ***11***) (17), and anti-tuberculosis (N-isopropylisonicotino-hydrazide,***12***) (18), they were also used as organic, inorganic, and analytical reagents.

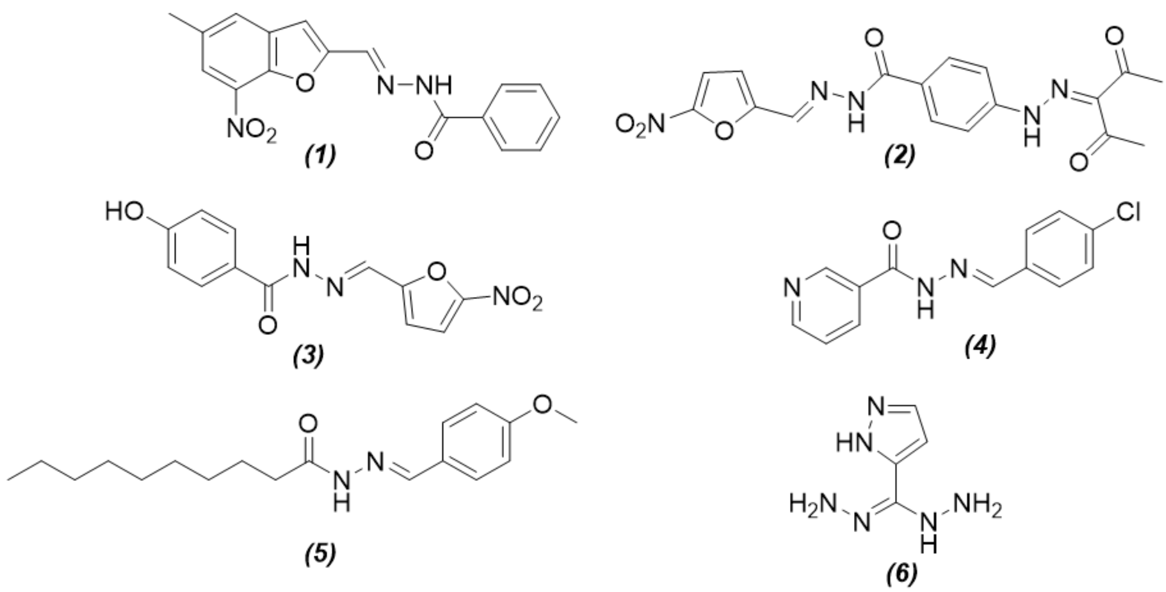


Figure 1: Some biologically important hydrazone derivatives

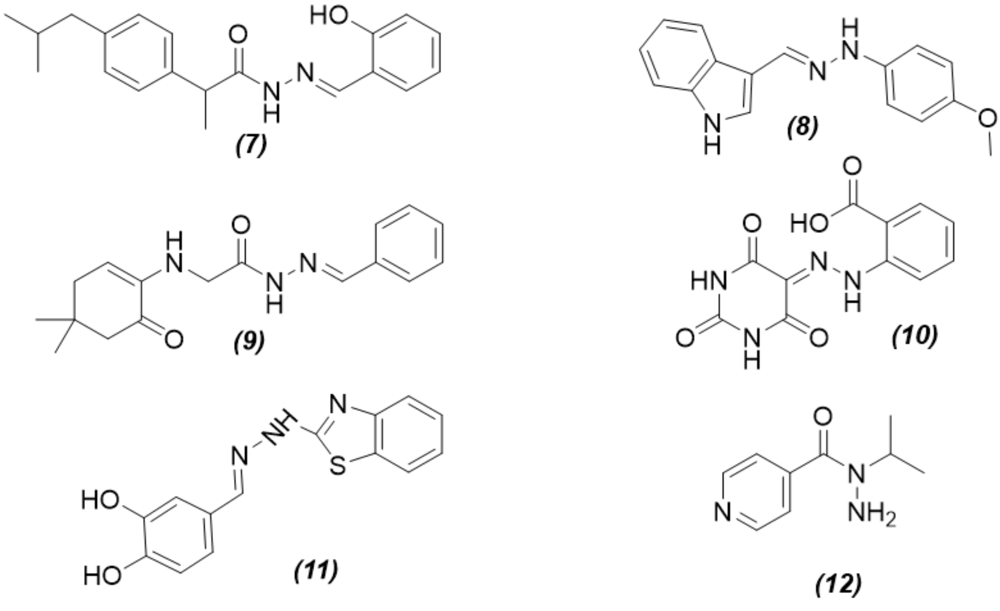


Figure 2: Biologically active hydrazone derivatives

Hydrazones are also used as plant growth regulators (2-((2-(benzo[d]oxazol-2-yl)-2-methyl-hydrazineylidene)methyl)benzoic acid, ***13***) (19), insecticides (podophyllotoxin-based hydrazone, ***14***) (20), pesticides (substituted nalidixic acid based hydrazones, ***15***) (21), corrosion inhibitors (ethylacetoacetate-[N-(3-hydroxy-2-naphthoyl)] hydrazone, ***16***) (22) etc. They are important an class of compounds for the synthesis of other heterocyclic compounds like Coumarin, Pyridine, Thiazole and Thiophene Derivatives (2-cyano-N'-(1-(pyridin-3-yl)ethyl-idene)acetohydrazide ***(17)*** (23), and polymer initiators (acetophenone *t*-butylhydrazone, ***(18)*** (24).

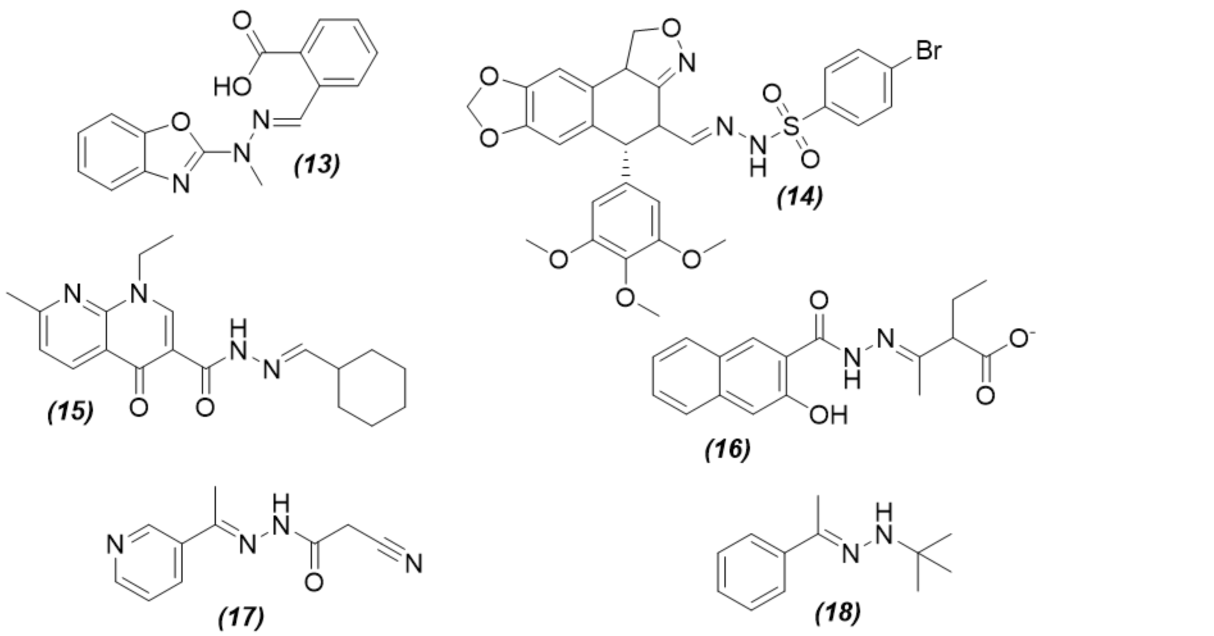


Figure 3: Hydrazone derivatives as polymer initials, corrosion inhibitor, pesticidal, insecticidal

ANALYTICAL APPLICATIONS

Hydrazone is very important class of analytical reagents used for the spectroscopic determination of different metal ions in food, environmental, pharmaceutical, and biological samples. These are also used for organic compounds' determination like glucose, carbonyl compounds, estrogen, etc. in blood, urine, cell culture, and pharmaceutical samples. Hydrazone derivatives are also used as corrosion inhibitors for nickel, copper, and many others in acidic and basic media. They are widely used for dyeing purposes for cotton, nylon, etc., chemosensors, polymer initiators, sensitizers, pH sensors for detection of microbes, and waste water treatment.

Spectrophotometric Agents

Hydrazone derivatives are not only extensively used for the detection of metal ions in water, alloys, soil and pharmacological samples but are also used for determination of anions like cyanide ion, fluoride ions, etc. via spectrophometric method. Hydrazone containing different heteroatom like S, O, N or presence of -OH, -C=O, -N-H, -COOH groups form stable compounds with metal ions and anions as compared to others. Hydrazone derivatives form soluble metal complexes when worked on in very small amounts and are capable of detecting metal ions in micro or nanograms.

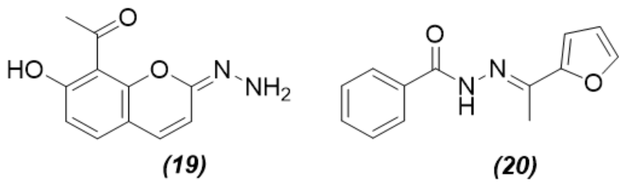


Figure 4: Hydrazone derivatives for spectrophotometric determination of metals.

Spectrophotometric determination of Cu (II) and Ni (II) in pharmaceutical samples was performed by 7-Hydroxy-8-aceto-coumarin hydrazone ***(19)*** at pH 4.5 and 5.5, respectively (25). 2-acetylfuran benzoyl-hydrazone ***(20)*** was prepared by Saleem Basha in 2017 and used for spectrophotometric Cu (II) determination in liver cells, vegetable oil, soil, cauliflower, and water samples as a greenish yellow colored complex at pH 6.5 with a detection limit ranging between 1.02 and 10.2 µg/ml (26). (Figure 4)

All the hydrazone derivatives that were used as spectrophotometric agents and the established conditions like color of complex, pH range, λ_{max} and detection limit in ppm are presented in **Table 1**. In this table, hydrazone reagents used for the detection of metals or anions via spectroscopic methods from the period of 1971 to 2021 were described.

Table 1: Important Hydrazone derivatives worked as Spectrophotometric Agents.

Spectrophotometric reagent	Sample	Metal ion	pH	Color of complex	Detection range (ppm)	$λ_{max}$ (nm)	Ref
3,5-Dimethoxy-4-hydroxybenzaldehyde isonicotinoyl-hydrazone	Alloy	Ni(II)	8.5-9.5	Yellow		386	(27)
	Alloy samples, hydrogenation catalyst samples and real water samples	Pd(II)	5.5	Bright yellow	0.1064-2.1284	382	(28)
	Monazite sand	Th(IV)	3.0	Yellow	0.580-5.80	390	(29)
	Synthetic mixtures, certified reference materials, water samples and pharmaceutical samples	Au(III)	4.0	Orange	0.197-1.97	386	(30)
	Beer, wine, vegetables and milk	Cu(II)	8.0-9.5	Bright yellow	0.317-3.17	494	(31)
Diacetylmonoxime-4-hydroxybenzoyl-hydrazone	Synthetic alloy	Pb(II)	10.0	Bright yellow	0.414-10.360	440	(32)
2-pyridinecarb-aldehyde 2-(5-nitro)pyridyl-hydrazone	Steel	Ni(II)	6.0	Red	0.05	475 & 507	(33)
	----	Fe(III)	7.0	Yellow	0.20–1.45	420	(34)
2,4-dihydroxy-benzaldehyde isonicotinoyl hydrazone	Alloy sample, zirconium sand and micro granite rock sample	Zr (IV)	1.5	Golden yellow	0.4-4.0	410	(35)
	Alloys and steel samples	Ti (IV)	1.0-7.0	Reddish brown	0.09- 2.15	430	(36)
	Synthetic samples and ores	Os (VIII)	5.0	yellow	0.95- 11.41	393	(37)
	Water and pharmaceutical samples	Zn(II)	6.0-8.0	greenish yellow	0.06- 1.6	390	(38)
	Monazite sand	Th(IV)	2.0-8.0	yellowish orange	0.3- 7.0	415	(39)
	Portable water samples	Fe(II)	7.0	Yellow	0.1-1.5	395	(40)
	Steel samples	Ti (IV) Mo (VI)	1.5 1.5	Red Golden	0.36-3.8 0.3- 6.0	560 445	(41)

Spectrophotometric reagent	**Sample**	**Metal ion**	**pH**	**Color of complex**	**Detection range (ppm)**	**λ_{max} (nm)**	**Ref**
	& in alloys			yellow			
	Silicate and carbonate minerals	Al(III)	5.5	Yellow	0.03-0.40	395	(42)
o-hydroxybenz-aldehyde isonicotinoyl hydrazone	---	Ga (III)		Yellow	0.2-1.6	390	
	---	In (III)	6.2	Yellow	0.3-2.5	380	(43)
	---	Co (II), Zn (II), Mn (II), Ni (II) Cd (II)	8.4	Yellow	---	390-420	(44)
3,4-dihydroxybenz-aldehyde isonicotinoyl hydrazone	Water	V(V)		Yellow	0.5-5.3	400	
		Cr(IV)	5.5		0.7-7.7	360	(45)
		Ti(IV)	3.5	Yellow	0.5-4.2	370	(46)
5-bromo-salicylaldehyde isonocotinoyl hydrazone	Water, hydrogenat ion catalyst and alloy	Pd(II)	1.0-5.0	Brown	0.4-11	445	(47)
	Soil and steel	Cr(VI)	6.0	Brown	0.16-3.90	430	(48)
	Eenvironm ental, phosphate rocks and fertilizer samples	U(VI)	5.0	Yellow	0.119-1.071	395	(49)
N'-(2-hydroxybenz-ylidene)-3-oxobutane-hydrazide	Synthetic mixtures and alloys	Ti(IV)	2.0	Reddish orange	1.75- 17.57	500	(50)
Diacetylmonoxime benzoylhydrazone	Alloys and synthetic mixtures	Ni(II)	8.0-10.0	---	0.12-2.58	362	(51,52)
		Cu(II)	8.0-11.0	---	0.2-2.54	346	
		Fe (II)	6.25	yellow	0.11-2.24	360	(53)
		Hg (II)	10.5	Orange	1-12	361	(54,55)
o-hydroxypropio-phenone isonicotinoyl hydrazone	---	U(IV)	3.0	Yellow	0.47-17	380	(56)
2-hydroxy-l-naphthaldehyde isonicotinoyl hydrazone	Synthetic mixtures	U(IV)	3.0	Orange red	0.2-33	430	(57)
2-Hydroxy-1-naphthalene carboxaldehyde phenyl hydrazone	Synthetic and commercial samples of alloy or ores (Hematite, steel, Fefol, Autrin, binary mixtures of Fe+Mg and Fe+Zn),	Fe (III)	6.0	Orange red	1-7	510	(58)
	Synthetic and commercial samples	Cu(II)	9.2	Yellow	1-10	360	(59)

Spectrophotometric reagent	**Sample**	**Metal ion**	**pH**	**Color of complex**	**Detection range (ppm)**	**λ_{max} (nm)**	**Ref**
	Alloys, steel, synthetic mixtures	Co(II)	8.4		1-10		(60)
2,5-Dihydroxyacetophenone benzoic hydrazone	Alloy and plant leaves	Cu(II)	Acidic	Yellow	0.3-6.0	400	(61)
1-((1E,4E)-4-((2-aminoethyl)imino)naphthalen-1(4H)-ylidene)-2-(2,4-dinitro-1λ^5-phenyl)hydrazin-1-ium	Soil, water, urine, human hair, goat liver, plant material, steel and alloy samples	V(V)	Basic	Red	0.02 - 3.5	495	(62)
2-hydroxy-1-naphthaldehyde-p-hydroxybenzoichydrazone	Water (river, tap, and rain), soil, pharmaceutical samples, wheat, orange, rice, tomato, banana, blood and urine	Fe(II)	5.0	Reddish brown	0.055-1.373	405	(63)
		Co(II)	6.0	Yellow	0.118-3.534	425	
	Environmental, Leafy vegetable, and Biological Samples	V(V)	4.0	Deep yellow	0.101-1.121	430	(64)
	Water, ore, fertilizer, and gas mantle samples	Th(IV)	6.0	Yellow	0.464-6.961	415	(65)
		U(IV)	6.0	Reddish brown	0.476-7.14	410	
	Nickel based alloy samples and geological samples	Y(III)	8.5	Yellow	0.044-2.222	410	(66)
	Plant, pharmaceutical, water and alloy samples.	V(V)	4.0	Deep yellow	0.050-1.935	430	(67)
		Pd(II)	4.0	Greenish yellow	0.022-2.021	430	
Diacetyl monoxime isonicotinoyl hydrazone	Rock, in pitchblende ore samples and synthetic samples	U(VI)	3.25	Yellow	1.19-14.28	364	(68)

Spectrophotometric reagent	Sample	Metal ion	pH	Color of complex	Detection range (ppm)	λ_{max} (nm)	Ref
	Synthetic alloys	Au(III)	4.5	Yellow	1.97-9.85	361	(69)
	Synthetic samples of alloy and in Monazite sand sample	Th (IV)	4.0-6.0	Yellow	1.16-13.12	352	(70)
	Synthetic alloys	Hg(II)	5.5	Yellow	1.003-12.3	351	(71)
	Synthetic mixtures,	Ga (III)	3.0-6.0	Green	0.002002	376	(72)
	biological samples	Ni(II)	8.0-9.0	Yellow	0.495-3.09	387	
	and alloys	Al(III)	7.0-8.0	Yellow	0.392-2.452	370	
	Alloys	Mo(VI)	5.0	Greenish yellow	0.48-5.76	346	(73)
pyridine-2-acetaldehyde salicyloylhydrazone	Synthetic samples, pharmaceutical samples and in high speed steel	Co(II)	1-4	Yellow	0.5-7.0	415	(74)
	Beer, wine, garlic, Tobacco and water samples	Fe(III)	2.5-3.0	Green	2.7-16.0	640	(75)
	Steel and alloys	V(V)	4.7	Yellow	0.5-2.0	415	(76)
	Synthetic mixtures, alloys, water and soil samples	Pb (II)	8.6-9.3	Yellow green	1.5-6.2	380	(77)
	Synthetic mixtures, catalysts and in ores	Pd(II)	2.0-4.25	Yellow	0.5-3.0	425	(78)
	Synthetic mixtures alloys and a pharmaceutical sample.	Sb(III)	2.9	Yellow	1.5-5.0	405	(79)
pyridine-2-carboxaldehyde 2-hydroxybenzoylhydrazone	Binary mixtures, multicomponent mixtures and in monazite sand	U (VI)	3.5-4.6	Yellow	1.0-5.6	375	(80)
	Eye Drops and	Hg(II)	8.8-10.0	Yellow	0.5-5.8	385	(81)

Spectrophotometric reagent	**Sample**	**Metal ion**	**pH**	**Color of complex**	**Detection range (ppm)**	**λ_{max} (nm)**	**Ref**
	Ayurvedic Medicines						
	Alloys and drug samples	Bi(III)	2.0-3.0	Yellow	0.7-4.3	380	(82)
N',N''E,N',N''E)-N',N''-(2,2'-(propane-1,3-diylbis(sulfanediyl))bis(1-(4-chlorophenyl)-ethan-2-yl-1ylidene))bis(2hydroxybenzohydrazide)	Water, food, medicinal plants and in synthetic samples	Co(II)	7.0	Orange	0.059-0.59	380	(83)
5-Bromosalicyl-aldehyde Thiosemicar-bazone	Grape leaves and aluminum based alloy samples	Cu(II)	4.5	Greenish yellow	0.31 – 6.35	390	(84)
phenylglyoxal mono(2-pyridyl)hydrazone	Tap water, mineral water and in cooking salt	Zn(II)	7.2-8.5	yellow-orange	0.05-0.6	464-470	(85)
N-oxalylamine-(salicylaldehyde hydrazone)	Aluminum and nickel alloy	Ga(III)	3.8	greenish yellow	0.003- 0.227	382	(86)
	Mineral water	Al(III)	3.7	---	0.005- 0.16	387 & 474	(87)
4-Hydroxy 3, 5-dimethoxy benzaldehyde-4-hydroxybenzoyl-hydrazone	Synthetic alloy sample	Fe(II) Fe(III)	4.0 5.0	Yellow Yellow	0.139-1.396 0.279-2.79	400 380	(88)
	Edible oil, plant sample and in alloy samples	Ni(II)	9.0	Yellow	0.117-0.528	408	(89)
	Hydrogenation catalyst, synthetic alloy and in water samples	Pd (II)	3.0-4.0	Brown	0.106-1.06	373	(90)
	Beer, Wine, Biological materials and alloy samples	Cu(II)	8.0-9.0	Yellow	0.063-0.635	382	(91)
3-Methoxy-salcilaldehyde-4-hydroxybenzoylhydrazone	Synthetic matrix, alloy samples and edible oils	Cu(II) Ni(II)	5.0-6.0 5.0-6.5	Yellow Yellow	0.1271 – 2.5418 0.1174 – 2.9410	390 425	(92)
Cinnamaldehyde-4-hydroxybenzoylhydrazone	Tealeaves, vehicle exhaust, vitamin B_{12} and in some alloy	Co(II)	9.0	Yellow	0.029-0.294	393	(93)

Spectrophotometric reagent	**Sample**	**Metal ion**	**pH**	**Color of complex**	**Detection range (ppm)**	**λ_{max} (nm)**	**Ref**
	samples						
	Plant sample, edible oil and in alloys	Ni(II)	8.0-9.0	Yellow	0.146-1.46	400	(89)
	Tannery effluent, synthetic water and chrome liquor samples	Cr(VI)	4.0	Brown	0.078-0.780	440	(94)
	Food stuffs, pharmaceutical samples and alloys	Mo (VI)	3.0-4.0	Green	0.047-0.479	404	(95)
	Hydrogenation catalyst samples, synthetic alloy samples and in water samples.	Pd (II)	4.0-5.0	Brown	0.106-1.064	375	(90)
benzil-α-monoxime isonicotinoyl hydrazone	Pipe water, bore water and municipal water samples	Pb (II)	10.0-11.0	Yellow	0.41-13.26	405	(96)
dipyridylglyoxal mono(2-pyridyl)-hydrazone	Pharmaceutical samples, multivitamins, hormones and Hidropolivit mineral	Cobalt (II)	3.0-7.0	Orange red	0.15-2.0	510	(97,98)
salicylaldehyde benzoyl hydrazone	Steel, alloys, water, human blood, urine, apple, egg, soil and synthetic mixtures	Cu(II)	1.21-2.58	Greenish yellow	0.001-10	404	(99)
benzil mono-(2-pyridyl) hydrazone	Steel and alloy samples	Co(II)	Basic	Red	0.0061-0.061	535	(100)
Benzil mono(2-quinolyl)hydrazone	---	Cu(II)	6.0	Red	0.3-3.0	520	(101,102)

Spectrophotometric reagent	Sample	Metal ion	pH	Color of complex	Detection range (ppm)	λ_{max} (nm)	Ref
2,4-dimethoxy benzaldehyde-4-hydroxy benzoylhydrazone	Pharmaceutical samples (Zingisol, Insulin Zinc Suspension and in Biocosules Z)	Zn (II)	10.0-11.0	Yellow	0.163-1.96	466	(103)
2,4-dihydroxy benzophenone benzoic hydrazone	Simulated rock samples	Ce (IV)	10.0	Orange red	0.7-7.0	400	(104)
5-Bromo-2-hydroxy-3-methoxybenzaldehyde-p-hydroxybenzoic hydrazone	Alloy samples, industrial water, drinking water, plant samples and in vegetable oil	Ni(II)	5.5-7.5	Green	0.117-2.64	440	(105)
	In alloys, steel and in water	Ti (II)	2.0-7.0	Orange	0.241-2.87	390	(106)
2-(3′-sulfobenzoyl)-pyridine benzoyl-hydrazone	Natural water	Fe(II)	7.0-9.0	Blue	0-4	646	(107)
N,N′-Oxalyl-bis(salicylaldehyde Hydrazone)	Water	Al(III)	4.7	Yellow	0-0.2	390	(108)
N-cyanoacylacet-aldehyde hydrazone	Water	Au(III)	3.0-7.0	Blue	1-30	550	(109)
p-dimethylaminoben-zaldehyde isonicotinoyl hydrazone	---	Hg(I) Hg(II)	3.5	Orange yellow	---	---	(110)
4-Hydroxy benzaldehyde-4-bromophenyl hydrazone	Water and alloy sample	Ni(II)	4.0	Red	0.01-1.0	497	(111)
3-methylbenzothiazolin-2-one hydrazone	Drugs	Ce(IV)	4.2	Orange	4.0-80.0	450	(112)
2-(4-biphenyl)-imidazo[1,2-]pyrimidine-3-hydrazone	---	Cu(II)	4	Green	---	430	(113)
Glutaraldehyde phenyl hydrazone	Water, soil, biological samples	Pb, Cr, Cd, As	5.6-7.5	---	---	387 (Cd) 395 (As) 395 (Pb) 360 (Cr)	(114)

Chemosensors

Chemosensors are non-toxic nano-sized organic molecules or receptors that produced a detectable change for sensoring analyte (usually metal ions or small molecules) using fluorescence spectroscopy (115). These chemosensors not only detect toxic and dangerous chemicals in the external and internal environment of the human body but also transmit that information to the nervous system to expel these toxins from body. For this purpose, a large number of organic molecules can be used but hydrazone derivatives containing thiol, carboxylic group gained more importance. Some important hydrazone derivatives used as chemosensors are presented below in **Table 2.**

Organic compound detector

Hydrazone derivatives are efficiently used for detection of organic compounds (Figure 5) like glucose, aromatic amines, hetero-atomic compounds, azo dyes, active methylene compounds, etc., in blood, urine, and pharmaceutical samples via spectroscopic and chromatographic methods.

Alzweiri and coworkers established a unique method for the spectrophotometric determination of glucose in biological samples by derivatization of glucose with 2,4-dintrophenyl hydrazine ***(21)*** (154).

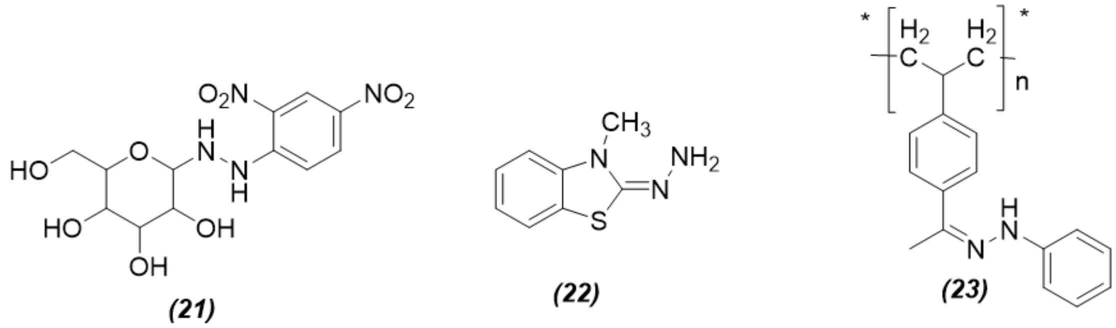


Figure 5: Hydrazone derivatives as organic compounds detector.

3-Methylbenzthiazolinone-2-hydrazone ***(22)*** was used as an analytical reagent for determination of phenols (155), azo dyes, Schiff bases, stilbenes (156), aliphatic aldehydes from fumes and polluted air (157), carbazole in air (156), aromatic amines (158), imino heteroaromatic compounds (158), heterocyclic bases, heteroaromatic compounds, compounds with active methylene groups (159), Rutin (160), glyoxal (161), phenolphthalein in pharmaceutical products (162), metaxalone (163), dabigatran etexilate mesylate (163), total estrogens in urine (164), determination of formaldehyde and acetaldehyde in methanol and ethanol (165), oxcarbazepine in pharmaceuticals, sulpha drugs in blood and urine samples (166,167), cannabinoids on thin-layer chromatography plates (168), free salicylic acid in aspirin (169), dobutamine hydrochloride (170) and carbonyl compounds in pharmaceutical samples (159) via different spectroscopic and chromatographic techniques.

By this method, 99.93% of phenol from waste water was removed by polystyrene hydrazone ***(23)*** by solid-phase extraction method prepared by acetylation of waste polystyrene with phenyl hydrazine (171).

For the determination of atmospheric ozone in very low concentrations up to 0.02 ppm and carbonyl compounds from mixtures, 2-Diphenylacety-1,3-indandione-1-hydrazone ***(24)*** was used as a spectrofluorometric reagent (172,173).

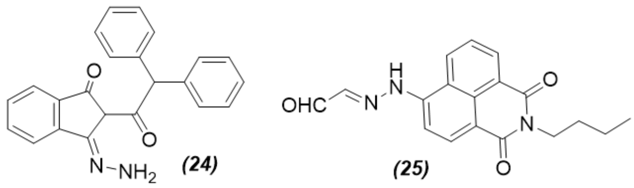


Figure 6: Fluorescence detecting hydrazone derivatives

Naphthalimide-based glyoxal hydrazone ***(25)*** is used for biological imaging of cysteine and homocysteine inside living cells via fluoresce spectroscopy with a color change from dark to green (174).

Table 2: Some Important Hydrazone reagents used as chemosensors

Chemosensor Name	**Sample**	**Analyte**	**LOD (M)**	**Color change**	**Fluorescence color**	**Tested media**	**Em/ ex (nm)**	**Ref**
1-phenyl-3-methyl-5-hydroxy-pyrazole-4 benzoyl(fluorescein)-hydrazone	---	Cu^{2+}	2.0 x10^{-3}	Colorless → Yellow		DMSO/ H_2O	337/287	(116)
Benzil mono(2-phen-yl)hydrazone	Biomedical & environmental	Cu^{2+}	8.25 $\times10^{-8}$	Colorless → Pink		THF/H_2O	490	(117)
Salicylaldehyde hydrazone derivatives	Living cells (MCF-7 calls)	Al^{3+}	1.5×10^{-7}	Colorless → blue		DMF/H_2O	450/390	(118)
2-((E)-(((E)-2-hydr-oxybenzylidene)hydrazineylidene)methyl)-6-methoxy-4-nitrophenol	Liver cells	Cu^{2+}	18x10^{-8}	Colorless → light yellow	Green	H_2O	570/400	(119)
	Biological system	Al^{3+}	7.45x10^{-8}	Yellow → colorless	Green	CH_3OH	545/400	
ethyl (E)-5-((2-(2-(2-hydroxyethyl)-1,3-dioxo-2,3-dihydro-1H-3a1λ5-benzo-[de]isoquinolin-6-yl)hydrazineylidene)methyl)-2,4-dimethyl-1l2-pyrrole-3-carboxylate	HeLa cells	Cu^{2+}	3x10^{-6}	Yellow → red		CH_3CN/ H_2O	620/480	(120)
(3a^{1}S)-2-butyl-7-(2-((Z)-1-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)ethylidene)-hydrazineyl)-3a,3a^1-dihydro-1H-benzo[de]isoquinoline-1,3(2H)-dione	Real sample	Cu^{2+}	1.58	Yellow → Colorless		THF/H_2O	520/412	(121)
4-methyl-N'-(ferrocene-2-ylidene)benzenesulfonohydrazide		Cu^{2+}	2.66×10^{-5}	Pale yellow → yellow green		CH_3CN		(122)
		Hg^{2+}	7.60x10^{-6}	Pale yellow → Red		CH_3CN		
(E)-3-(1-(2-(benzo[d]thiazol-2-yl)hydrazineylidene)ethyl)-7-(diethylamino)-2H-chromen-2-one	HeLa tumor cells (Cervical cancer cells)	Cu^{2+}	4x10^{-8}	Yellow → wine red		1%DMSO	572/420	(123)
7-(diethylamino)-3-((E)-(((E)-(2-hydroxynaphthalen-1-yl)methylene)hydrazineylidene)methyl)-2H-chromen-2-one	human breast adenocarcinoma	Cu^{2+}	2x10^{-4}		Green	CH_3OH/ H_2O	574/487	(124)

Chemosensor Name	Sample	Analyte	LOD (M)	Color change	Fluorescence color	Tested media	Em/ ex (nm)	Ref
	cells (MCF-7 cells)							
3-(2-((3-Hydroxy-5-(hydroxymethyl)-2-methylpyridin-4-yl)methylene)hydrazinyl)-1,2-benzothiazole 1,1-dioxide	Biological system	Al^{3+}	$6x10^{-7}$	White → yellow	Blue	DMSO/ H_2O	468/399	(125)
2-(3a,7a-dihydro-1H-benzo[d][1,2,3]triazol-1-yl)-N'-((8-hydroxyquinolin-5-yl)methylene)-2λ²-ethanehydrazide	Biological system	Mg^{2+}	$6.9x10^{-3}$	Blue → green	bright yellow	CH_3CN	525/395	(126)
2- aminoquinolin-3-yl-phenyl hydrazone	---	Fe^{3+}	8.22 x 10^{-6}	---		C_2H_5OH	423/246	(127)
N-(quinolin-8-ylmethylene)acetohydrazide	In HeLa cells	Zn^{2+}	$8.93x10^{-2}$		bright yellow	C_2H_5OH	525/360	(128)
N-((8-hydroxy-5-quinoline aldehyde acetylhydrazone)-benzoaza-15-crown-5	Biological system	Mg^{2+}	$7.87x10^{-5}$	Colorless → Yellow		C_2H_5OH	520/370	(129)
	germinated potato, bitter almond and in tap water	CN^-	$3.57x10^{-7}$	Colorless → Yellow	bright yellow	DMSO/ H2O	498/355	
3',6'-bis(diethylamino)-2-(((3-hydroxypyridin-2-yl)methylene)amino)spiro[isoindoline-1,9'-xanthen]-3-one	Biological system	Cu^{2+}	$3.63x10^{-7}$	Colorless → purple	White	DMSO/ H2O	492/373	(130)
		Cu^{2+}	$2.5x10^{-8}$	Colorless → pink		H_2O/ CH_3CN	585/520	(131)
3',6'-bis(diethylamino)-2-((2-(2-(2-methoxyethoxy)-ethoxy)benzylidene)amino)spiro[isoindoline-1,9'-xanthen]-3-one	HeLa cells	Hg^{2+}	$1.5x10^{-7}$	Colorless → purple	Orange	CH_3CN	590/558	(132)
(Z)-N'-(1-(2,4-dihydroxy-phenyl)ethylidene)-2,2,2-trifluoroacetohydrazide		Cu^{2+}	$1x10^{-5}$	Colorless → yellow	Bright green	DMF	500/400	(133)
2-(((3H,4'H-1l3,1'l3-[2,2'-bithiophen]-5-yl)methyle-ne)amino)-3',6'-bis(diethyl-amino)spiro[isoindoline-1,9'-xanthen]-3-one	Human epithelial adenocar	Hg^{2+}	$2.31x10^{-8}$	Colorless → purple	Blue	EtOH/ H2O	590/544	(134)

Chemosensor Name	Sample	Analyte	LOD (M)	Color change	Fluorescence color	Tested media	Em/ ex (nm)	Ref
	cinoma (HeLa) cells							
3',6'-bis(diethylamino)-2-((2-hydroxy-5-(1,2,2-triphen-ylvinyl)benzylidene)amino)spiro[isoindoline-1,9'-xanthen]-3-one	---	Cu^{2+}	10^{-6}	Colorless → purple		EtOH/H_2O	550/-	(135)
2-(((3H,4'H-1l3,1'l3-[2,2'-bithiophen]-5-yl)methylene)-amino)-3',6'-bis(diethyl-amino)spiro[isoindoline-1,9'-xanthene]-3-thione	Human epithelial adenocarcinoma (HeLa) cells	Hg^{2+}	$3.10x10^{-9}$	Colorless → purple	Pink	EtOH	593/390	(136)
3',6'-bis(diethylamino)-2-((piperidin-2-ylmethyl)-amino)spiro[isoindoline-1,9'-xanthen]-3-one	Caco-2 cells	Cu^{2+}	0.137	Colorless → red	Orange	CH_3CN	573/520	(137)
N-(3′,6′bis(diethylamino)-3-oxospiro[isoindoline-1,9′-xanthen]-2-yl)-3-oxo-3-ferrocenylpropanamide	HeLa cells	Cu^{2+}	$1.0x10^{-6}$	Colorless → purple	Orange red	ethanol/ H2O	595/550	(138)
2-(hydrazineylidenem-ethyl)pyren-1-ol	HeCaT cells	Zn^{2+}	$3x10^{-4}$	Colorless → yellow	Green	CH_3CN	527/450	(139)
3',6'-bis(diethylamino)-2-((2-mercaptobenzylidene)amino)spiro[isoindoline-1,9'-xanthen]-3-one	Nematode *Caenorhabditis elegans*	Hg^{2+}	$1x10^{-9}$	Colorless → pink	Red	CH_3CN/ H_2O	580/510	(140)
1-phenyl-3-methyl-5-hydroxypyrazole-4-carbalde-hyde(benzoyl)hydrazone		Cu^{2+}	$1.0x10^{-6}$			CH_3CN	305/406	(141)
3',6'-bis(diethylamino)-2-((furan-2-ylmethylene)-amino)spiro[isoindoline-1,9'-xanthene]-3-thione	Rat Schwann cells	Hg^{2+}	$5x10^{-4}$	Colorless → pink	Orange	H_2O–DMF	564/500	(142)
4-nitro-2-[(phenylhydra-zoimino)methyl]phenol		F^-	0.02–0.2 $x10^{-4}$	Colorless → yellow	Yellow	CH_3CN		(143)
4-nitro-2-[(4-nitrophenylhydra-zoimino)methyl]phenol		F^-	0.02–0.2 $x10^{-4}$	Colorless → orange	Yellow	CH_3CN		

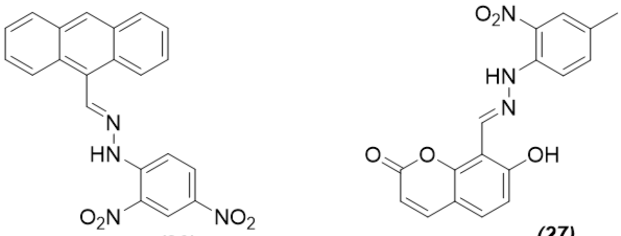
Chemosensor Name	**Sample**	**Analyte**	**LOD (M)**	**Color change**	**Fluorescence color**	**Tested media**	**Em/ ex (nm)**	**Ref**
N',N'''-((1E,1'E)-(((4-((E)-(2-(1-hydroxy-2-naphthoyl)-hydrazineylidene)methyl)phenyl)azanediyl)bis(4,1-phenylene))bis(methaneylylidene))bis(3-hydroxy-2-naphthohydrazide)	Human cervical cancer (HeLa) cancer cell lines	Cu^{2+}	---	---	---	H_2O/ CH_3CN	470/450	(144)
3,3'-((1E,1'E)-(((1E,1'E)-(((4-((E)-(((E)-(1-hydroxy-naphthalen-2-yl)methylene)-hydrazineylidene)methyl)phenyl)azanediyl)bis(4,1-phenylene))bis(methaneylylidene))bis(hydrazine-2,1-diylidene))bis(methaneylylidene))bis(naphthalen-2-ol)	Human cervical cancer (HeLa) cancer cell lines	Cu^{2+}	---	---	---	H_2O/ CH_3CN	430/405	(144)
2-(((1E,2E)-but-2-en-1-ylidene)amino)-3',6'-bis-(ethylamino)spiro[isoindoline-1,9'-xanthen]-3-one	Water, soil	Pd^{2+}	$1.80x10^{-7}$	Colorless → pink	Yellow	EtOH/H_2O	555/505	(145)
2-hydroxy-benzaldehyde benzoyl-hydrazone	biological and environmental sample	Cu^{2+}	$5.6x10^{-6}$	---	---	MeOH/ H_2O	490/424	(146)
Methyl Pyrazinylketone Benzoyl Hydrazone	---	Al^{3+}	10^{-7}		Green	Ethanol	506/390	(147)
3',6'-bis(diethylamino)-2-((2-hydroxybenzylidene)amino)spiro[isoindoline-1,9'-xanthen]-3-one	---	Cu^{2+}	---	Colorless → pink		CH_3CN	576/520	(148)
(E)-(2-((2-(2,4-dinitrophenyl)hydrazineylidene)methyl)phenyl)diphenylphosphine oxide	----	F^-	2×10^{-5}	Yellow → pink		CH_3CN	514/379	(149)
N-(2-(-(2-(-3,4-dihydroxy-6-(hydroxymethyl)-5-(-3,4,5-trihydroxy-6-(hydroxymethyl) tetrahydro-2H-pyran-2-yloxy) tetrahydro-2H-pyran-2-yl) hydrazono) methyl)-4-(-phenyldiazenyl) phenyl) acetamide	Water	CN^-	$1.29x10^{-6}$	Colorless → purple		MeOH/ H_2O	----	(150)
(E)-2-(2-(2,4-dinitrophenyl)hydrazineylidene)-1,2-diphenylethan-1-one	Real water and simulated urine samples	CN^-	10^{-7}	Yellow → Red		CH_3CN/ H_2O		(151)
1-((Anthracene-9-yl)-methylene)-2-(4-nitrophenyl)hydrazine		F^-	$4x10^{-5}$	Yellow → green		DMSO	571/493	(152)
N, N-diethylamino-3-acetyl coumarin with 2-hydrazinobenzothiazole	HeLa cells	Cu^{2+}		Yellow → orange	Green	DMF	536/420	(123)

Chemosensor Name	**Sample**	**Analyte**	**LOD (M)**	**Color change**	**Fluorescence color**	**Tested media**	**Em/ ex (nm)**	**Ref**
N-(3-methoxy-2-hydroxybenzylidene)-3-hydroxy-2-naphthahydrazone	Water	Zn^{2+} Cd^{2+}	Zn (9.85×10^{-9} M) Cd (1.27×10^{-7} M)	---	Yellow (Zn) Red (Cd)	THF/H_2O	365/440 645/430	(153)

LOD= limit of detection; Em= emission; Ex= excitation;

Water detectors

Hydrazone – acetate derivatives ***(26)*** derived from 9-anthracenealdehyde and 7-hydroxy-coumarin-8-carboxaldehyde were used as for Chromogenic signaling (detection) of water contents in water miscible organic solvents like THF and acetonitrile by Y.H. Kim *et al* in 2012 (175). Anthracene-based hydrazone ***(27)*** was found to be more sensitive to water content as compared to 7-hydroxycoumarin hydrazone and showed a visible color change from red to yellow with a detection limit of 0.037 and 0.071% in both solvents (175).



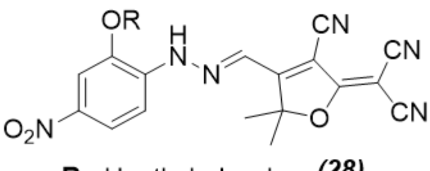
(26) *(27)*

Figure 7: Water-monitoring hydrazone derivatives.

Microbes detectors

Most of the hydrazone derivatives have different colors in acidic and basic media as well as in neutral ones. This property of hydrazones is very useful for microbe detection in food and pharmaceutical samples (Figure 8).

Recently, Khattab and coworkers introduced Tricyanofuran hydrazone derivatives ***(28)*** as pH sensors for detection of microbes which alkalize the environment, like *S. aureus, B. subtilis, E. coli, and P. aeuroginosa*. The color change from yellow to blue to red indicates the pH change from acidic to neutral to basic. These pH sensors were also used to detect microbes in food packages and pharmaceutical samples (176-178).



(28)

Figure 8: Microbe detecting hydrazone derivatives.

Sorbents

Some modified hydrazone derivatives are widely used as sorbents in ion exchange chromatography or in Sol-gel process for separation of ions in synthetic mixtures, natural water, ash coal, petroleum products, and pharmaceutical samples. Such hydrazones work as low cost resins with high productivity, are highly stable and can be used many times with the same sorption capacity listed in **Table 3.**

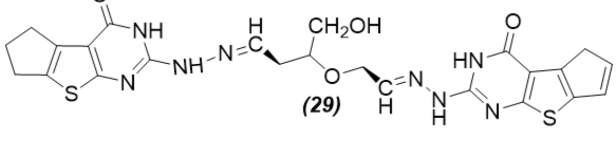
Organic Collectors in Flotation

Flotation is the separation process of toxic metal ions in trace amounts, for this purpose many hydrazone derivatives worked as organic collectors. These form hydrophobic aggregates with metal ions that float with the help of air bubbles produced on the surface of solution by slight shaking of floatation cell. Many important hydrazones used as organic collectors are summarized in **Table 4.**

Sewage Water Treatment

Sewage water is commonly known as wastewater, which contains a large amount of contamination mainly coming from household and industrial waste. This wastewater contains several heavy metals like mercury, arsenic, cadmium, chromium, lead, thallium, and nitrogen compounds like ammonia, nitrite, and nitrates. Many physical, chemical, and biological processes are now used for sewage water treatment, but most of these are very costly and time consuming.

Cellulose hydrazone derivatives were obtained by the reaction of dialdehyde cellulose and 2-hydrazino-3,5,6,7 tetrahydrocyclopentanethieno[2,3-d]-pyrimidin-4(4H)-one ***(29)*** used as a polymer for sewage water treatment and the removal of several heavy metal ions. The synthesized derivatives were used for production of clean water with less side effects. These derivatives not only had ability to remove iron and chromium up to 73.91 % but also chlorine up to 50 % **(192).**



(29)

Figure 9: Hydrazone for sewage water treatment.

Table 3: Some widely used hydrazones as sorbents.

Sorbent	**Separated Ion**	**Sample**	**pH**	**LOD (ppb)**	**Eluent**	**Recovery %**	**Ref**
1-(3,4-Dihydroxy-benzylidine)-2-acetylpyridinium chloride hydrazone	Fe^{3+}	Waste water, sea water, lake water, food oil, petroleum products, pharmaceutical sample	3.0	1.0	0.5 M HCl	ˆ100	(179)
	Cr^{3+}	Waste water	6.0	13.3	0.1 M HCl	ˆ100	(180)
	Cr^{6+}	Waste water	2.0	10.0	3.0 M HCl	ˆ100	(180)
	Ga^{3+}	Synthetic mixture of mercury, aluminum, cobalt, copper, zinc & lead	2.5-3.0	20	0.5 M HCl	98	(181)
	In^{3+}		2.5-3.0	13	5.0 M HCl	98	(181)
	Tl^{3+}		2.0	20	2.0 M HCl	95	(181)
acenaphthenequinone-[N-[(2,4-dinitrophenyl)]-hydrazone	La^{3+}	Lake water, rain water, river water	4.0	---	0.1 M HNO_3	97	(182)
1-[(bromomethyl)-(phenyl)methyl]-2-(2,4-dinitrophenyl) hydrazine	Ag^{+}	Tap water, drain water	5.0			99	(183)
4-hydroxy-N'-[(E)-(2-hydroxyphenyl)methylidene]benzohydrazide	Biogenic amines	Orange juice, ketchup, budu, soy sauce.	9.0	20-60	---	99.7	(184)

LOD= limit of detection in ppb

Polymer initiators

Polymer synthesis is the process in which small molecules (monomers) covalently combined to form giant molecules that are more stable as compared to initiators. Many organic molecules are used for this purpose, but hydrazone derivatives gave the highest yields and the best results among them (Figure 10).

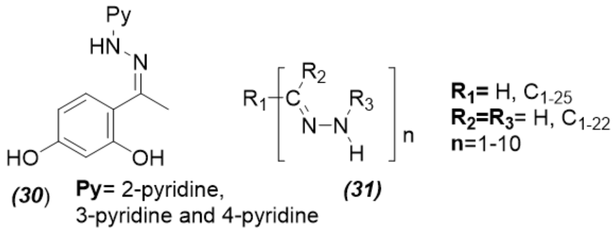


Figure 10: Polymer initiating hydrazone derivatives

Nakanishi et al. and Masuda et al. used pyridine hydrazone derivatives ***(30)*** as a suitable and useful initiator or starting material for the synthesis of synthetic polymers or hydrazone polymers (193,194).

Hydrazone derivatives ***(31)*** were used as initiators for high yield polymerization of acrylamide, acrylic acid or styrene at a temperature -10-98°C with yield up to 77% (24). Similarly, acylhydrazone derivatives were also used as starting materials for acylhydrazone polymers (195).

A series of six hydrazone derivatives ***(32)*** were prepared by Singh and coworkers and used for the synthesis of hydrazone functionalized epoxy polymers by the conversion of hydrazone derivatives into epoxide to form hydrazone polymer (Figure 11). These polymers showed high nonlinear optical properties (196).

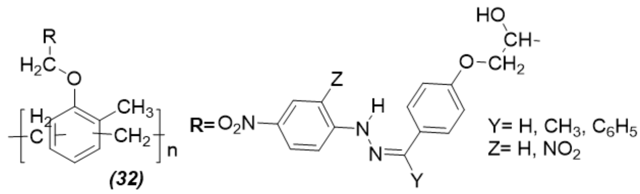
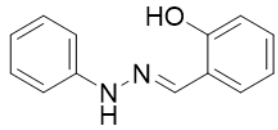


Figure 11: Hydrazone as epoxy polymer

Indicators

Salicylaldehyde phenylhydrazone **(33)** prepared by Love and Jones from simple and cheap starting material was used as an indicator for the titration of organometallics, including Grignard reagent, providing a clear and accurate end point from yellow to golden orange or red (Figure 12) (197).



(33)

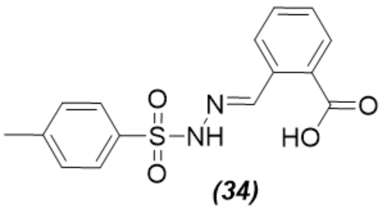
Figure 12: Hydrazone as indicator.

Table 4: Hydrazones used as organic collectors in flotation.

Organic collector	Surfactant	Metal ion	Tested Sample	pH	Recovery %age	HOL	Ref
1-acetylpyridinium chloride-4-phenylthio-semicarbazide	Oleic acid	Hg^{2+}	Natural water samples of Mansoura city	6.8	ˆ100	$1x10^{-3}$	(185)
4-acetylpyridine-[N-(3-hydroxy-2-naphthoyl)]hydrazone	Oleic acid	Ni^{2+}	Water	7.0	ˆ100	$4x10^{-4}$	(186)
1-(amino-N-(pyridine-3-yl)methanethio)-4-(pyridine-2-yl)thiosemi-carbazide	Oleic acid	Hg^{2+}	Sea water, lake water, Nile water, distilled water	5.0	100	$1x10^{-3}$	(187)
thiophene-2-carboxaldehyde-[N-(3-hydroxy-2-naphthoyl)]-hydrazone	Oleic acid	Ni^{2+}	Water	7.0	ˆ100	$4x10^{-4}$	(186)
salicylaldehyde-[N-(3-hydroxy-2-naphthoyl)]-hydrazone	Oleic acid	Ni^{2+}	Water	7.0	ˆ100	$4x10^{-4}$	(186)
p-anisaldehyde-[N-(3-hydroxy-2-naphthoyl)]hydrazone	Oleic acid	Ni^{2+}	Water	7.0	ˆ100	$4x10^{-4}$	
ethylacetoacetate-[N-(3-hydroxy-2naphthoyl)]-hydrazone	Oleic acid	Ni^{2+}	Water	7.0	ˆ100	$4x10^{-4}$	
(E)-2-(2-(dimethylamino)-1λ^3,3λ^2-thiazol-4-yl)-N'-(2-hydroxybenzylidene)acetohydrazide	Oleic acid	Zn^{2+}	Water	7.0	96	$1x10^{-3}$	(188)
4-(2-pyridyl-azo) resorcinol mono sodium mono hydrate	Oleic acid	Cu^{2+}	Water, drug	3-5	95	$2x10^{-5}$	(189)
Oxalyl-bis(3,4-di-hydroxy-benzylidene) hydrazone	Oleic acid	ZrO^{2+}	Sea water, underground water, lake water, tap water, Nile water	3.0	99.7	$1x10^{-5}$	(190)
2-(2-(4-hydroxy-3-methoxybenzylidene) hydrazinyl)-2-oxo-N-phenylacetamide	Oleic acid	Cu^{2+}	---	7.0	98	$1x10^{-3}$	(191)
2-(2-(2-hydroxy-3-methoxybenzylidene) hydrazinyl)-2-oxo-N-phenylacetamide	Oleic acid	Cu^{2+}	---	7.0	99	$1x10^{-3}$	(191)

Catalyst

2-Carboxybenzaldehyde-p-Toluenesulfonyl Hydrazone ***(34)*** was used as an efficient catalyst in coupling reaction (Figure 13) of benzaldehyde, piperidine, and phenylacetylene with 1,4 dioxane as a solvent for the preparation of 1-(1,3-diphenylprop-2-yn-1-yl)piperidine at 120 ˚C (198).



(34)

Figure 13: Hydrazone as catalyst for organic coupling reaction.

Corrosion Inhibitors

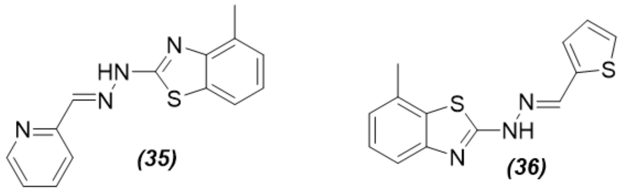
Corrosion is the degradation process of metals to form oxides, sulfides, or hydroxides. Many organic compounds like pyrimidine, imidazole, oxazole, triazole, amino acids and hydrazone are common organic corrosion inhibitors used to prevent or delay corrosion process of metals like copper, nickel, iron, and tin. Among all the organic compounds hydrazone gained much importance due to heteroatom nitrogen and oxygen. Some important hydrazone derivatives that worked as good corrosion inhibitors are presented in **Table 5.**

Ionophores

Ionophores are ion carriers and have tendency to bind, shield, and facilitate transportation of metal ions across the membrane (Figure 14). Ganjali and coworkers used pyridine-2-carbaldehyde-2-(4-methyl-1,3-benzothiazol-2-yl) hydrazone ***(35)*** and thiophene-2-carbaldehyde-(7-methyl-1,3-benzothiazol-2-yl)hydrazone ***(36)*** as suitable neutral ionophore for the preparation of Er (III) and Tm (III) membrane sensor at pH 2.5-12.0 and 3.0 - 12.0, respectively, with lower detection limits 5.0 $\times 10^{-6}$ M and 8.0x10^{-6} M. (218,219).

Dyes and Pigments

Nowadays, various hydrazones are used as stable dyes and pigments with a visible color change at different pH levels due to C=N-N linkage or presence of carbonyl group. Such dyes are not only used for dying polyester, silk, cotton, or nylon but are also used as sensitizers or for dying purposes in dye sensitized solar cells due to their broad absorption band.



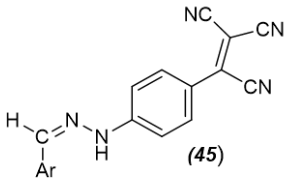
(35) ***(36)***

Figure 14: Hydrazone derivatives as ionophore for inner transition metals

Tricyanofuran hydrazone derivatives *(37)* were tested as pigments on polyester fibers to give orange-red, yellow and orange shades with λ_{max} 485 nm, 478 nm, and 463 nm, respectively, by Khattab and coworkers (220).

A series of heterocyclic hydrazone dyes ***(38-44)*** (Figure 15) were prepared from 2-amino-3-cyano-4-chloro-5 formyl-thiophene and five pyridine-2,6-dione based coupling components by Qian and coworkers. These hydrazone derivatives display distinct colors: yellow, purple, pink, and grey on five common fibers like Polyester, Nylon, Silk, Wool, and Cotton at pH 7.0 and 8.5 (221).

Al-Sehemi and coworkers synthesized different hydrazone dyes ***(45)*** (Figure 16) by the reaction of aromatic aldehydes with phenyl hydrazine. These hydrazones were further reacted with tetracyanoethylene to obtain violet colored dyes and supposed to be low-cost, efficient, and stable DSSC due to their smaller HOMO-LUMO energy gaps (222,223). Percentage efficiency for ***45*** was increased by 3.12 % at incident power 50 mW/cm^2. Due to high EA, it had high tendency to generate free electrons and holes (222,224-226).



(***45***)

Ar= phenyl, p-Cl-benzene, p-Br-benzene, p-NO_2-benzene, Naphthaline, Anthracene, 2-(methoxymethyl)phenol, 3,4,5-trimethoxybenzne, 3-ethoxy, 4-hyroxybenzene

Figure 16: Hydrazone derivatives as dyes in DSSC

Ping Shen at el synthesized and used a series of N, N-diphenyl-hydrazone dye as efficient sensitizers (Figure 17) for production of DSSC with maximum conversion efficiency of up to 5.83 % (227). A series of metal free hydrazone based dyes *(46)* were synthesized from cheap materials without any expensive catalyst and used as DSSC by Urnikaite at el. The highest solid-state device conversion efficiency for these hydrazone dyes was 3.8-4.5 % with FF % 64-72% under 100 mW cm^{-2}, AM 1.5G (228-230). In 2020, Al-Sehemi et al. synthesized some promising dyes CHMA, CDBA, and AMCH *(47)* for DSSC (231).

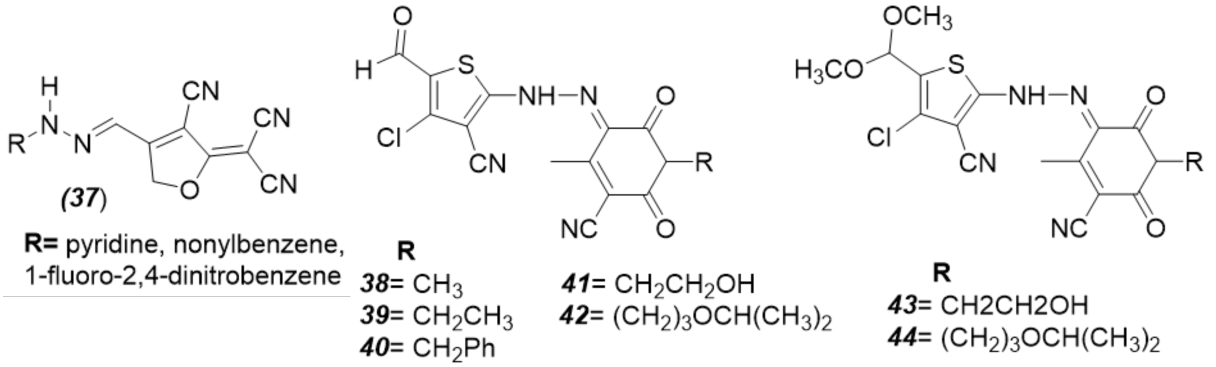


Figure 15: Hydrazone derivatives as dyes.

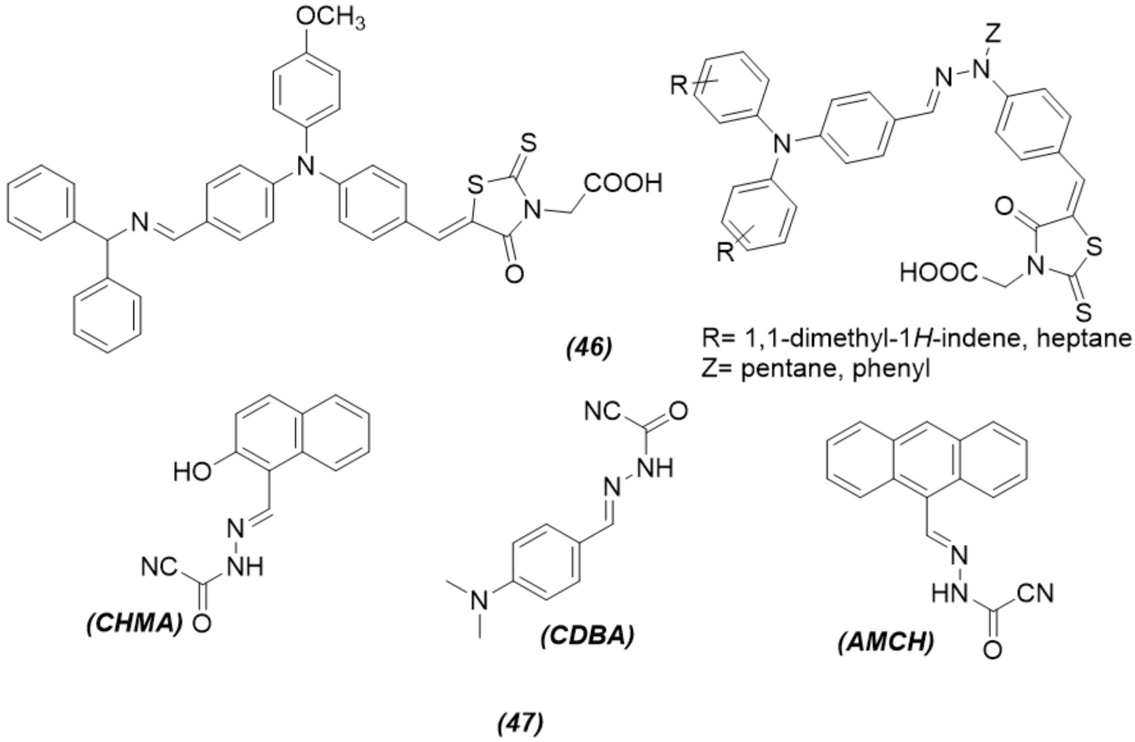


Figure 17: Hydrazone based dye sensitizers.

Nanoparticle synthesizer

3-thiopropionylhydrazones ***(48)*** of mono and di-saccharides were prepared by Vasileva *et al.* and used for the synthesis of silver glycol-nanoparticles in ultrasonic bath with average particle size of 15–40 nm while hydrazine hydrate was used as reductant (232).

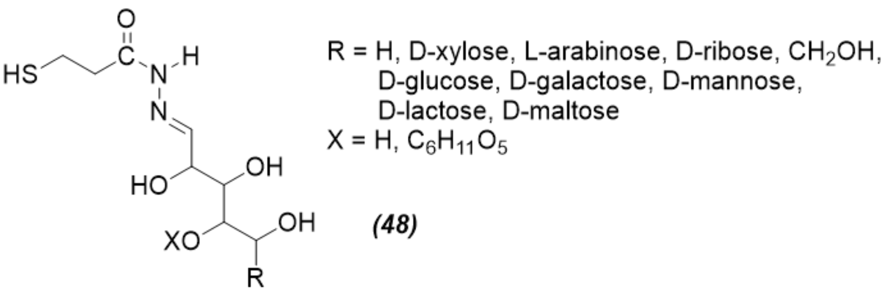


Figure 18: Hydrazone derivatives as nanoparticle synthesizer.

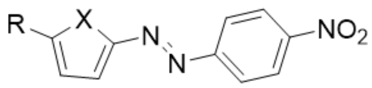
Table 5: Some important hydrazones that worked as good corrosion inhibitors

Corrosion inhibitors	Material	Medium	Conc. of inhibitor M	Inhibition efficiency (%)	Ref
(9H-fluoren-9-ylidene)hydrazine	Carbon steel	1.0 M H_2SO_4	10^{-1}	95.08	(199)
(2,7-dichloro-9H-fluoren-9-ylidene)hydrazine	Carbon steel	1.0 M H_2SO_4	10^{-1}	93.44	(199)
3-[8-(trlfluoromethyl)quinolin-4-yl]thlo]-N'-(2,3,4-trihydroxy-benzylidene)propano hydrazide	Mild steel	0.5 M H_2SO_4	$11.1x10^{-4}$	97.6	(200)
2,7-dibromo-9H-fluoren-9-ylidene)hydrazine	Carbon steel	1.0 M H_2SO_4	10^{-1}	89.34	(199)
(2,7-dinitro-9H-fluoren-9-ylidene)hydrazine	Carbon steel	1.0 M H_2SO_4	10^{-1}	84.42	(199)
2-hydroxyacetophenone-3-aminobenzoyl hydrazone	Copper	3N HNO_3	10^{-5}	70.0	(201)
3-hydroxybenzalde-hyde, 2-hydroxy-benzoyl hydrazone	Aluminum	2N HCl	$5x10^{-4}$	92.0	(202)
benzyl monophenyl hydrazone-N-cetyloxycarbonyl-ethyltaurate	Carbon steel	5% H_2S	$1x10^{-4}$	56	(203)
4-bromobenzalde-hyde, 2-hydroxy-benzoyl hydrazone	Aluminum	2N HCl	$5x10^{-4}$	92.0	(202)
Nitrobenzaldehyde G-T	C-steel	2 M HCl	$5x10^{-4}$	95.21	(204)
p-Hydroxybenzaldehyde G-T	C-steel	2 M HCl	$5x10^{-4}$	84.15	(204)
Thiophen-2-carboxaldehyde-[N-(3-hydroxy-2-naphthoyl)]-hydrazone	Nickel	2 M HCl	$1.5x10^{-5}$	59.3	(22)
bis-(o-methoxybenzaldehyde)-thiocarbodihydrazone	Copper	3.5% NaCl	$1.5X10^{-3}$	61	(205)
2-Acetophenone [N-3-hydroxyl-2-naphthoyl hydrazone]	Carbon steel	0.5 M H_2SO_4	$7X10^{-5}$	59	(206)
Furfural-isobutroyl hydrazone	Carbon steel	3 M H_3PO_4	$11x10^{-6}$	79.5	(207)
Furfural 4-methoxybenzoyl-hydrazone	Carbon steel	1 M H_3PO_4	$11x10^{-6}$	47	(208)
4-(N,N-dimethylamino) benzaldehyde nicotinic acid hydrazone	Mild steel	1M HCl	$6x10^{3}$	94.91	(209)
(E)-2-((2,3-dimethylphenyl)-amino)-N'-(thiophen-2-ylmethylene)-benzohydrazide	Mild steel	1M HCl	$5x10^{-3}$	92	(210)
(E)-2-((2,3-dimethylphenyl)-amino)-N'-(furan-2-ylmethylene)benzohydrazide	Mild steel	1M HCl	$5x10^{-3}$	88	(210)
2-((2,3-dimethylphenyl)amino)-N′-((1E,2E)-3-phenylallylidene)-benzohydrazide	Mild steel	1 M HCl	$5x10^{-3}$	97	(211)
(E)-2-((2,3-dimethylphenyl)-amino)-N′-(4-hydroxybenzy-lidene)benzohy-drazide	Mild steel	1 M HCl	$5x10^{-3}$	94	(211)
N′-(3-phenylallylidene) benzohydrazide	Mild steel	1 M HCl	$2x10^{-3}$	97.43	(212)
2-heterocarboxaldehyde-2′-pyridyl-hydrazones	Aluminum	2 M HCl	---	85	(213)
N-benzylidene-benzohydrazide	Mild steel	1 M HCl	$2.23x10^{-3}$	97.32	(212)
3-(cyano-dimethyl-methyl)-benzoic acid thio-phen-2-ylmethylene-hydrazide	Mild steel	0.5 M HCl	$2x10^{-3}$	91.2	(214)
3-(cyano-dimethyl-methyl)-benzoic acid furan-2-ylmethylene-hydrazide	Mild steel	0.5 M HCl	$2x10^{-3}$	86.7	(214)
2-(2-[2-(4-Pyridylcabonyl)-hydrazono]methyl-phenoxy)-acetic acid	Mild steel	Sea water	2.8×10^{-4}	85.4	(215)
4-(4′-benzoylhydrazine)-pyridine-carboxaldehyde hydrazone	N80 Steel	1 M HCl	$1x10^{-3}$	93.6	(216)
N′-[4-(diethylamino)-benzylidine]-3-[8-(trifluoromethyl)-quinolin-4-yl]thio-propano hydrazide	Mild steel	0.5 M H_2SO_4	$2x10^{-4}$	94.7	(217)

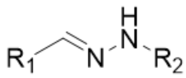
Nonlinear optical devices

Nonlinear optical materials are those materials or organic compounds that describe the behavior of light in nonlinear medium (Figure 19). Such materials play a major role in modern technology in telecommunication, optical switching, data processing, ultra-short pulsed lasers, laser amplifiers, sensors, and many more.

Shing Wong et al. synthesized various hydrazone derivatives ***(49)*** from aromatic aldehydes and 4-methoxy-phenylhydrazine or 4-tolylhydrazine or 4-nitrophenylhydrazine and used them with powder test for second or third order nonlinear optical devices (233).



X= O, S
R= CH_3, H_3CO, H_3CS
(49)



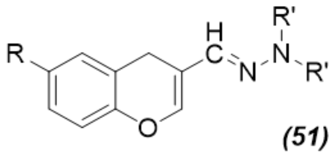
$\mathbf{R_1}$= pyrene, anthracene
$\mathbf{R_2}$= 4-flurobenzene, 2,4-difluorobenzene, 2,3,5,5-terafluorobenzene, 2,3,4,5,6-pentafluorobenzene
(50)

Figure 19: Hydrazone compounds used in nonlinear optical devices.

A series of eight anthracene hydrazone derivatives ***(50)*** were prepared and their third-order NLO performance was studied using the standard picosecond Z-scan technique in the open aperture mode by Wenjuan Xu at el. in 2018 (234). Similarly, 4-dimethylaminobenzaldehyde-4-nitrophenylhydrazone had promising non-liner optical properties (235).

Light emitting diodes

6-Alkyl-3-chromonealdehyde (2,2-dialkyl)hydrazone derivatives ***(51)*** were synthesized from 6-alkyl-3-chromonealdehydes and 2,2-dialkylhydrazones by Chung and Chang and were used as light-emitting diodes due to their green light emission (236).



(51)
R= CH_3, $CH(CH_3)_2$
R'= CH_3, C_6H_5

Figure 20: Hydrazone based light emitting diodes.

CONCLUSION

This review summarizes the analytical applications of hydrazone derivatives. These hydrazone derivatives are widely used as spectrophotometric agents not only for detection of metals in sand, soil, water, pharmaceutical samples, alloys, wine, beer, bread, oil, fruits, and vegetables, but also for the detection of organic compounds like carbazoles, aldehydes, ketones, carboxylic acids, salicylic acid, aspirin, aromatic amines, heterocyclic bases, and many more in drugs, food, air, blood, and urine samples. These are also used as organic collectors in flotation for collecting different metals from water, where oleic acid is used as surfactant. Nowadays, they are used as dyes in DSSC due to their broad absorption band, as chemosensors, especially in tumor cells due to their florescence property, as indicators and as microbe detectors due to their pH sensoring properties. Hydrazone derivatives are also used as corrosion inhibitors for nickel, iron, steel, copper, etc. Hydrazone derivatives have many binding sites due to which they have ability to bind metals via coordinate covalent bond and anions via covalent bond. This property makes them a unique class of compounds among all organic compounds. These types of compounds are used in light emitting diodes and due to nonlinear optical properties, are also used in lasers, telecommunication devices, and optical switching. Hydrazone derivatives produce stable colors that can't fade after long washing and are used as dying reagents for the dying of nylon, cotton, polyester, and silk. This review covers approximately 61 years of work on hydrazone's analytical applications with 236 references.

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