AN EXPOSITION ON SPECTROPHOTOMETRIC DETERMINATION OF PLATINUM GROUP METALS

TANU ARORA[1], NIVEDITA AGNIHOTRI [1], AND MOHAMMAD AZAM [2]*

[1]Department of Chemistry, Maharishi Markandeshwar (Deemed to be University), Mullana, Ambala-133207, India.
[2]Department of Chemistry, College of Science, King Saud University, Riyadh-11451, Kingdom of Saudi Arabia.

ABSTRACT

In the realm of analytical chemistry, transition metal complexes especially the platinum group metals (PGMs) are often used compounds. Strong chromophores, inflexible luminous structures, biological potential and electrochemical activity are characteristics of the platinum metal complexes. These features have prompted the creation and study of analytical techniques based on these metal complexes for the identification of different analytes in a variety of analytical applications. Even if there are a few broad recommendations accessible to forecast a reagent's potentialities for the given goal, these studies show that sensitivity and selectivity imparted by the reagent to the metal in respective complex must be established. The quest for novel reagents is an ongoing effort to the wide and varied need for new ways to identify and analyze the metal ions under the peculiar conditions. In light of the frightening and complicated issue of environmental contamination, the endeavor of developing new and innovative reagents as well as techniques for inorganic analysis of PGMs have particular relevance. Of the numerous methodologies, the UV/VIS spectrophotometric determination technique of the PGM complexes is of interest being reliable, easy to handle, quick, cost effective, selective and sensitive. The technique relies on the process of interaction between an analyte and the metal, which are then determined analytically. In light of the enrichment of platinum group metals, the purpose of this article is to outline current research in the methods of spectrophotometric determination of PGMs. The review will assist researchers in formulating and refining PGMs as workable candidates for applications in medicine, pharmacology, analysis and catalysis.

Keywords: Platinum Group Metals; Platinum metals; PGMs; Extraction; Spectrophotometric determination.

1. INTRODUCTION

The PGMs in form of their compounds/complexes are significant in several domains due to their distinct coordination chemistry. The Platinum Group Metals, also called platinoids, platidises, platinides, platinum group, platinum metals or platinum family, are a family of six elements *viz.* Ruthenium, Rhodium, Palladium, Osmium, Iridium and Platinum belonging to groups 8, 9 and 10 in the periodic table of elements that are structurally and chemically similar and known for their array of applications including industrial, medicinal and electronic. These are imperative noble metals known for their distinct chemical and physical properties [1-3]. Depending on their atomic numbers (or weights), the PGMs metals are sometimes divided into light platinum group metals (Ru, Rh, Pd) and heavy platinum group metals (Os, Ir, Pt) [4]. These can also be sub-divided as iridium-group platinum group elements (osmium, iridium and ruthenium) and the palladium-group platinum group elements (rhodium, platinum, palladium) based upon their behaviour in geological systems.

1.1 Discovery of PGMs

The English Scientist William Hyde Wollaston was the first to isolate pure platinum, palladium and rhodium in 1803-04; Smithson Tennant found pure iridium in 1803, as did N.Z. Vauquelin and A.F. de Fourcroy in France. In 1803 or 1804, Tennant also discovered osmium. The Russian chemist K.K. Klaus made the latest PGM, ruthenium, to be isolated in 1844. Palladium, rhodium and iridium are all named after their respective Greek origins. Palladium was given its name in honor of the asteroid, Pallas, since both objects were discovered about the same time. Rhodium receives its name from the hue of aqueous, acidic solutions of metal salts, which is taken from the word, rhodon, meaning rose. Osmium is derived from osme, which means scent, due to the unique aroma of its volatile tetraoxide and iridium comes from the term iris, rainbow like, due to the vast spectrum of colors that iridium salt solutions show. Ruthenium is named after Ruthenia, the Latin name for Russia and the last PGM, the Platinum which was first found in the sixteenth century in Columbia's Choco district, found its name originated from the word, platina in Spanish, meaning little silver [5-7].

1.2 The Principal PGM Sources

PGMs, low-prevalence elements, are primarily supplied by South Africa, with reserves estimated at 63,000 tons in 2020, followed by Russia, Zimbabwe, the US and Canada. Platiniridium is the naturally occurring platinum-iridium alloy; however, osmiridium is the known natural alloy of iridium and osmium. The platinum group metals can be either sulphur-loving or iron-loving and can also be pronounced as chalcophiles and siderophores, respectively. The common minerals of PGMs are-Tellurides, selenides, arsenides and antimonides. There are several significant sulphide minerals of Ru, Pd and Pt. The PGM deposits are indicated in Table 1 [8], where the deposits in Merenskey Reef are seen associated with iron, nickel and copper ores. The major source of the metals is Sudbury area in Canada where the metals are found as by-product of nickel and copper production. However, in general, the platinum group metals are known to exist together with their ratio variable with the ore location [9, 10].

1.3 Advantages of PGMs

Six noble metals with a white-silver hue make up the platinum group: ruthenium, iridium, osmium, palladium, platinum and rhodium. PGMs are grouped collectively in the periodic table of elements based on similar mineralization and characteristics. Without a question, the most well-known PGM is platinum due to its thermal stability as well as melting point [11]. The metal is compatible with biological systems and acts as an effective oxidation catalyst. Palladium is less common than platinum, yet it is nonetheless useful for a variety of chemical processes because of its special capacity to absorb hydrogen. With a high melting point and exceptional thermal stability, rhodium is also known to possess good catalytic properties . Iridium is an extremely rare metal that is resistant to corrosion. It is also highly stable both chemically and thermally, dense and compatible with life. Ruthenium possesses strong melting point and is an excellent alloying agent exhibiting good conductive and catalytic qualities. The densest and hardest metal, osmium is frequently used in combination with other PGMs and is another efficient catalyst and superb electrical conductor [1, 12, 13].

*Corresponding author email: nivagni11@gmail.com

Table 1: Platinum Group Metal Content (grams tonne^{-1}) in Ore Bodies

Location of PGMs Deposits	Ruthenium g/t	Rhodium g/t	Palladium g/t	Osmium g/t	Iridium g/t	Platinum g/t	Total PGM g/t
Canada							
Sudbury Complex	0.04	0.03	0.4	0.01	0.01	0.3	0.79
Lac-des lles	-	-	2.3	-	-	0.2	2.5
USA							
Stillwater Complex	0.36	0.6	11	-	0.21	3.3	15.47
Zimbabwe							
Hartely Complex	-	0.21	1.8	-	-	2.6	4.61
Russia							
Noril'sk	-	0.24	-	-	-	2.5	9.74
South Africa							
Merensky Reef	0.33	0.16	1.4	0.04	0.05	2.7	4.68
-East Bushveld	0.23	0.13	1.22	-	0.04	2.32	
-West Bushveld	0.63	0.28	1.6	-	0.14	3.6	
Platreef	0.14	0.12	1.9	0.03	0.04	1.9	4.13
-North Bushveld	-	0.08	1.1	-	-	0.82	2.0
UG2	0.45	0.34	1.3	0.05	0.13	2.0	4.27
-East Bushveld	0.76	0.45	2.06	-	0.18	2.42	
-West Bushveld	0.93	0.54	1.48	-	0.22	2.89	

The Platinum group elements show a diverse array of applications in the following industries: electronics, gas remediation, automotive industry, petroleum refining, fine chemical and ammonia manufacturing and the environment [8, 14]. However, the principal application of platinum group metals is in alloys and as catalysts in numerous industrial manufacturing. The PGMs being a part of luxurious lifestyle are used in jewellery making because of their property of thermal stability and corrosion-resistance [15].The medical field is highly enlightened with the application of PGMs [16-19]. The metal complexes have received a lot of interest recently from the medical world and from therapeutics treating terrible diseases like cancer due to the metals' propensity for organic substrates, their activity in redox reactions and their ability to exist in a variety of oxidation states. Because of the mentioned characteristics of metal complexes, platinum group based complexes have occasionally been used in the remedial field, giving them notable qualities in the subsequent field [20-22].

The wide range of applications for platinum group metals based complexes, including industrial, chemical, catalytic and electronic, as well as the potential to treat deadly diseases like cancer, make them highly valuable resources that require careful consideration and diligence to advance both the prosperity of these fields and the quality of healthcare in general [8]. In this context, attempts have occasionally been made to develop methods and procedures pertinent to the creation of novel compounds of the metals and also the protocols for figuring out their trace concentrations and hence the micro scale determination.

2. Determination of Platinum Group Metals

Trace analysis of metals has evolved significantly since World War II, driven by the need for high purity materials. It is a valuable tool in various industries, including food, environmental pollution and archeological research [23]. Trace amounts of metals and nonmetals are essential for biological processes as well, but toxic concentrations can pose a threat. In light of the variety and unique complexity in the structures of PGM compounds as well as the chemical changes they undergo in both natural and industrial systems, the coordination and analytical chemistry of the platinum metals is a distinct subject in chemistry. Trace element determination can be done using a variety of instrumental techniques. Among the most suitable analytical techniques that have been suggested thus far are gravimetric [24, 25], titrimetric [26], AAS [27], X-ray analysis [28, 29], nuclear [30, 31], potentiometry and voltammetry [32], inductively coupled plasma atomic emission spectrometry (ICP-AES) [33], inductively coupled plasma mass spectrometry (ICP-MS) [34], electrothermal atomic absorption spectrometry (ET-AAS) [35] and UV-VIS spectrophotometry [36]. Nonetheless, the expediency of the aforementioned methods for the direct determination of platinum metals is compromised by a number of shortcomings and deficiencies, such as cost-ineffectiveness, safety concerns and maintenance challenges. Therefore, it becomes necessary to create and discover a methodology that can withstand and overcome all of the shortcomings of the aforementioned approaches [37, 38]. Spectrophotometry is the most commonly used technique for trace metal determination since the very beginning, as it is simple and inexpensive method. Using appropriate purity reagents is crucial for sensitive spectrophotometric techniques. UV/VIS spectrophotometry, hence, has developed into a powerful analytical tool to address the demerits of the current methodologies.

Spectrophotometric Methods of Determination of PGMs

When compared to other applied analytical techniques, various organic reagents/ligands have been noted to be sensitive, cost-effective, precise and accurate when utilized for the trace level determination of the platinum metals employing a UV/VIS spectrophotometric methodology. As a result, a thorough and concise analysis of the existing spectrophotometric techniques is carried out on PGMs and provided below to determine the extent to which these methods satisfy the mentioned criteria.

2.1 Thiourea derivatives

Thiourea (Figure 1) and its derivatives have unique structural and electrical properties, making them useful in biological and non-biological sectors. These form hydrogen bonds and offer coordination sites as ligands, making them useful as chemosensors for identifying metal cations in biological, agricultural and environmental samples. Owing to its great sensitivity, selectivity and cheap cost of synthesis, thiourea and its derivatives are used as organic chemosensors, producing stable complexes with numerous cations including those with PGMs that are vital to different fields [39]. The spectrophotometric aspects of the different derivatives (Figure 2) have been collected together in the Tables 2a to 2d as below:

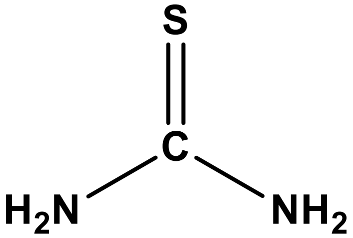

Figure 1: Thiourea

Table 2a: Spectrophotometric Determination of PGMs using Thiourea Derivatives as Ligands

Derivative used	Metal Detected	Aqueous conditions; Composition	Solvent; λ_{max} (nm)	Molar absorptivity ($Lmol^{-1}cm^{-1}$)	Comments	Reference
Ethylene thiourea (ETU)	Os (VIII)	1M H_2SO_4, pH 1.0; 1:3	Water; 490	16.87 x 10^4	Interferences of few ions masked using EDTA and fluoride	40
Ethyl thiourea	Os (III)	HCl; 2%$NH_4[Cr(CNS)_4(aniline)]$, acetone; 1:3	Acetone; 535-540	793.067	Less sensitive	41
N,N'-Diphenylbenzimidoyl Thiourea (DPB1TU)	Pd (II)	0.5M HCl; equilibration time 1 min.; 1:2	$CHCl_3$; 365	2.50 x 10^4	1 min. extraction time	42
N-octyl-N'-(sodium p-amminobenzenesulfonate)-thiourea (OPT)	Pd (II)	Buffer, pH 5.2, Heating at 50˚C for 6 min., CTMAB; 1:4	Water; 299	1.38 x 10^5	Heating at 50˚C for 6 min	43
N-(3,5-Dimethylphenyl)-N´-(4-Aminobenzene sulfonate) thiourea ((DMMPT)	Pt (IV)	Buffer, pH 3.8, colour development time 10 min., CTMB; 1:3	CH_2Cl_2; 755	9.51 x 10^4	Colour development time 10 min.	44
N-(3,5-Dihydroxylphenyl)-N´-(4-Aminobenzene sulfonate) thiourea (DHPABT)	Pt (IV)	5M HCl, Colour development time 10 min.; 1:2	Water; 760	1.01 x 10^5	Colour development time 10 min.	45
N-dodecyl-N´-(sodium-p-aminobenzenesulfonate) thiourea (DOPT)	Pd (II)	Buffer, pH 5.4, Heating at 100˚C, CTMB; 1:4	Water; 296.4	7.41 x 10^4	Heating at 100˚C required; Cu^{2+} interferes	46
N-(m-Methylphenyl)-*N´*-(sodium *p*-aminobenzenesulfonate)-thiourea (MMPT)	Pt (IV)	Buffer, pH 4.0, Heating at 90º C for 3min.; 1:3	Water; 754.4	8.58 x 10^4	Heating at 90º C for 3 min.	47

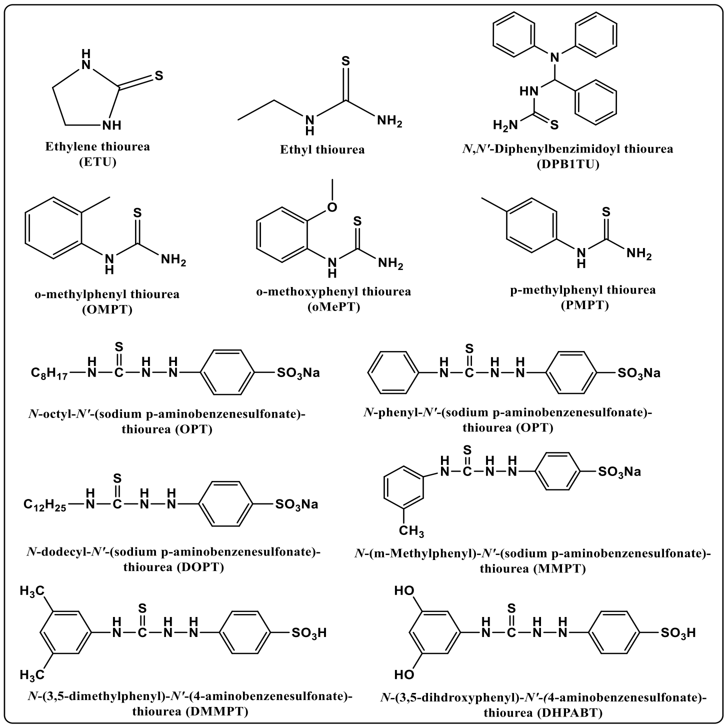

Figure 2: Thiourea derivatives as chromogenic ligands

Table 2b: Spectrophotometric Determination of PGMs using Thiourea Derivatives as Ligands

Derivative used	Metal Detected	Aqueous conditions; Composition	Solvent; λ_{max} (nm)	Molar absorptivity ($Lmol^{-1}cm^{-1}$)	Comments	Reference
o-methylphenylthiourea (OMPT)	Pd (II)	0.8M HCl, 5 sec. equilibration time; 1:1	$CHCl_3$; 340	2.85×10^3	Ag (I) interferes	48
	Pt (IV)	0.1M KI; 1:1:2	$CHCl_3$; 362	1.25×10^4	-	49
	Ru (III)	3M HCl; Heating for 5 minutes; 1:2	$CHCl_3$; 590	2.34×10^3	Heating on boiling water bath for 5 minutes	50
	Os (IV)	0.8M HCl; 1:1	$CHCl_3$; 514	1.86×10^3	Pd (II), Ir (III) interfere	51
	Rh (III)	Buffer, pH 5.4, Heating for 4 minutes; 1:2	$CHCl_3$; 320	9.76×10^3	Heating in boiling water bath for 4 minutes	52
	Ir (III)	0.6M HCl; 1:1	$CHCl_3$; 516	0.663×10^3	Pd (II), Os (VIII) interfere	53

Table 2c: Spectrophotometric Determination of PGMs using Thiourea Derivatives as Ligands

Derivative used	Metal Detected	Aqueous conditions; Composition	Solvent; λ_{max} (nm)	Molar Absorptivity ($L\ mol^{-1}cm^{-1}$)	Comments	Reference
o-methoxyphenyl thiourea (OMePT)	Pd (II)	1M HCl; 1:1	$CHCl_3$; 325	3.38×10^3	Ag (I) interferes	54
	Os (IV)	0.8M HCl; 1:1	$CHCl_3$; 518	2.12×10^3	Pd (II), As (III), Ir (III) interferes	55
	Ru (III)	3.4M HCl,Heating for 5 minutes; 1:2	$CHCl_3$; 640	2.34×10^3	Heating in boiling water bath for 5 minutes; Ir (III) interferes	
N-phenyl-*N′*-(sodium p-aminobenzenesulfonate)-thiourea (PPT)	Pt (IV)	Buffer, pH 4.0, CTMAB,5 min. heating at 80°C; 1:3	Water; 778.4	2.95×10^4	5 min. heating at 80°C in water bath; Cu (II) interferes	56
	Pd (II)	Buffer,pH 5.5, CTMAB,5 min. heating at 80^0C; 1:4	Water; 306.1	7.98×10^4	5 min. heating at 80°C in water bath ; interference was observed by Cu^{2+}	

Table 2d: Spectrophotometric Determination of PGMs using Thiourea Derivatives as Ligands

Derivative used	Metal Detected	Aqueous conditions; Composition	Solvent; λ_{max} (nm)	Molar Absorptivity ($Lmol^{-1}cm^{-1}$)	Comments	Reference
p-methylphenyl thiourea (PMPT)	Ru (III)	0.2M HBr, heating for 5min. at 70° C ; 1:1	$CHCl_3$; 600	2.31×10^3	5min. heating in boiling water bath at 70° C	57
	Ir (III)	0.1M $HClO_4$; 1:1	$CHCl_3$; 482	0.909×10^3	Pd(II) requires prior extraction	58
	Os (VIII)	0.45M $HClO_4$; 1:1	$CHCl_3$; 512	6.83×10^3	5 sec equilibration time	59
	Pt (IV)	0.03M KIO_3; 1:1	$CHCl_3$; 506	6.78×10^3	Os (VIII) and Ir (III) requires prior extraction	60
	Pd (II)	0.05M HBr,10 sec. equilibration time; 1:1	$CHCl_3$; 300	8.486×10^3	10 sec equilibration time	61

2.2 Thiosemicarbazones derivatives

Thiosemicarbazones (Figure 3) are employed as a chelating ligand in the production of metal complexes because of their adaptable donor sets, including nitrogen and sulphur [62]. These can coordinate in a variety of ways to produce coordination compounds with different metal ions. It is a condensed mixture of ketone or aldehyde and thiosemicarbazone [63]. Because of their bonding mechanisms and the presence of amide, imine and thione groups, which make them potential polydentate ligands, thio and phenyl thiosemicarbazones have drawn increasing interest in recent years [64]. Behaving as anti-retroviral, anti-microbial, anti-tubercular, anti-HIV, anti-fungal, anti-trypanosomal, anti-amoebic, anti-malarial, anti-viral, anti-tumor, anti-bacterial and cytotoxic substances, are a few of the biological characteristics of thiosemicarbazones. Due to their particular and selective coordination capabilities, thiosemicarbazones themselves have the potential to be used as metal ion for sensing and scavenging of metals. Their metal complexes have also been identified to have potential use in medical imaging [65]. The till date investigated PGM complexes using thiosemicarbazones as ligands (Figure 4) have been put under tables 3a-3d.

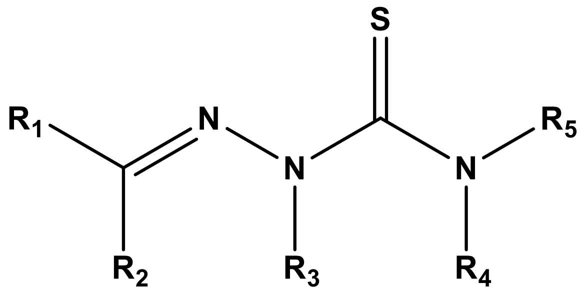

Figure 3: Thiosemicarbazones

Table 3a: Spectrophotometric Determination of PGMs using Thiosemicarbazone derivatives as Ligand

Derivative used	Metal Detected	Aqueous conditions; Composition	Solvent; λ_{max}(nm)	Molar Absorptivity (Lmol^{-1}cm^{-1})	Comments	Reference
p-[*N,N*-bis(2-chloroethyl) amino]Benzaldehyde thiosemicarbazone (CEABT)	Pd (II)	0.2M HCl, CEABT; 1:2	Water; 395	4.05 x 10^4	Cu(II) and Pt(VI) interfere	66
4-[*N,N*-(diethyl)amino] benzaldehyde thiosemicarbazone (DEABT)	Pt (IV)	Buffer, pH 3.0; 1:2	Water; 405	1.755 x 10^4	Cu(II) and Pd(II) interfere	67
Phthalaldehydic acid thiosemicarbazone (PAATSC)	Pd (II)	2M Buffer , pH 4.0, 1min. equilibration time; 1:10	$C_6H_{12}O$; 355	5.1 x 10^4	1min. equilibration time	68
Benzildithiosemicarbazone (BDTSC)	Pd (II)	Buffer, pH 2.5, 30 sec. equilibration time 1:1	$(CH_3)_2CHCH_2CCH$; 395	3.018 x 10^4	Ag(I) requires prior extraction	69
2,6-Diacetylpyridine bis-4-phenyl-3-thiosemicarbazone (2, 6-DAPBPTSC)	Pd (II)	Buffer, pH 4.0, 1min. equilibration time; 1:1	$C_5H_{12}O$; 410	1.156 x 10^4	1min. equilibration time	70
Isonitroso p-nitroaceto phenone thiosemicarbazone (HINATS)	Pd (II)	1M CH_3COOH, 1min. equilibration time; 1:1	$CHCl_3$; 410	910	1min. equilibration time, Less sensitive	71
Pyridoxalthiosemicarbazone (PTSC)	Pd (II)	Buffer , pH 2.0; 1:2	Water; 420	1.63 x 10^4	-	72
N-Ethyl-3-carbazole carbaxaldehyde thiosemicarbazone (ECCT)	Pd (II)	Buffer, pH 4.0, 3 min. equilibration time; 1:1	C_4H_9OH; 410	1.647 x 10^4	3 min. equilibration time	73
3,4-dihydroxy-5-methoxy Benzaldehyde thiosemicarbazone (DHMBTSC)	Ru (III)	Buffer , pH 2.0, Triton X-100; 1:1	Water; 425	2.73 x 10^4	-	74

Table 3b: Spectrophotometric Determination of PGMs using Thiosemicarbazone derivatives as Ligand

Derivative used	Metal Detected	Aqueous conditions; Composition	Solvent; λ_{max}(nm)	Molar Absorptivity (Lmol^{-1}cm^{-1})	Comments	Reference
Phenanthraquinone monothiosemicarbazone (PTS)	Ru (III)	Buffer, pH 5.2-6.7, Heating for 2 hours; 1:2	Water; 660	9843.81	Heating in water bath for 2 hours, Cu(II) and Rh(III) interfere	75
	Rh (III)	0.2M $C_8H_5KO_4$, Heating for 90 min.; 1:2	Water; 510	7900	90 minutes heating on water bath is required, Ru(III), Pd(II) and Cu(II) interfere	76
	Os (VIII)	CH_3OH, pH 6.8-8.5; 1:3	Water; 530	15280	Ni(II), Cu(II), Co (II), Ru (III), Rh (III) and Ir(III) interfere	77

Table 3c: Spectrophotometric Determination of PGMs using Thiosemicarbazone derivatives as Ligand

Derivative used	Metal Detected	Aqueous conditions; Composition	Solvent; λ_{max}(nm)	Molar Absorptivity (L mol^{-1}cm^{-1})	Comments	Reference
2-(5- Bromo-2- oxoindolin-3-ylidene) hydrazine carbothioamide (HBITSC)	Ru (III)	Buffer, pH 4.6, Digested for 25min., Equilibration time 1 min.; 1:3	$CH_3(CH_2)_4OH$; 505	9855.95	Digested for 25min. in boiling water bath; Equilibration time 1 min.	78
	Pd (II)	2M HCl, Equilibration time 1 min.; 1:2	$CH_3(CH_2)_4OH$; 520	7450	Equilibration time 1 min.	79
	Os (IV)	Buffer , pH 4.5, Digested for 30 min.; 1:2	$CH_3(CH_2)_4OH$; 565	10000	Digested for 30 min. in boiling water bath	80
	Rh (III)	Buffer , pH 5.5, Digested for 30 min., Equilibration time 1 min.; 1:3	$CH_3(CH_2)_4OH$; 495	3345	Digested for 30 min. in boiling water bath; Equilibration time 1 min.	81
	Pt (IV)	Buffer, pH 4.6, Digested for 30 min., Equilibration time 1 min.; 1:2	$CH_3(CH_2)_4OH$; 505	8452.53	Digested for 30 min. in boiling water bath	82
	Ir (III)	Buffer, pH 6.5, Digested for 30 min.; Equilibration time 1 min.; 1:3	$CH_3(CH_2)_4OH$; 500	1153.35	Digested for 30 min. in boiling water bath; Equilibration time 1 min.	83

Table 3d: Spectrophotometric Determination of PGMs using Thiosemicarbazone derivatives as Ligand

Derivative used	Metal Detected	Aqueous conditions; Composition	Solvent; λ_{max}(nm)	Molar Absorptivity ($Lmol^{-1}cm^{-1}$)	Comments	Reference
2-hydroxy-3-methoxy Benzaldehyde thiosemicarbazone (HMBATSC)	Ru (III)	Buffer, pH 2.5; 1:1	Water; 390	0.964×10^4	-	84
	Pd (II)	Buffer, pH 3.0; 2:3	Water; 380	2.198×10^4	-	85
Piperonal thiosemicarbazone (PATS)	Pd (II)	0.5M HCl; 1:2	Water; 363	3.80×10^4	Cu(II),Hg(II) and Pt(II) interfere	86
	Pt (IV)	0.2M H_2SO_4; equilibration time 10 min.; 1:2	Water; 360	3.24×10^4	Cu(II), Hg(II),Au(III)and Pd(II) interfere	87
Pyridoxal-4- phenyl-3-thiosemicarbazone (PDPTSC)	Pd (II)	Buffer, pH 3.0, equilibration time 1 min.; 1:1	C_6H_6; 460	2.20×10^4	Equilibration time 1 min.	88
	Pt (IV)	Buffer , pH 3.5	$CHCl_3$; 460	3.561×10^3- 7.641×10^3	Less sensitive method	89

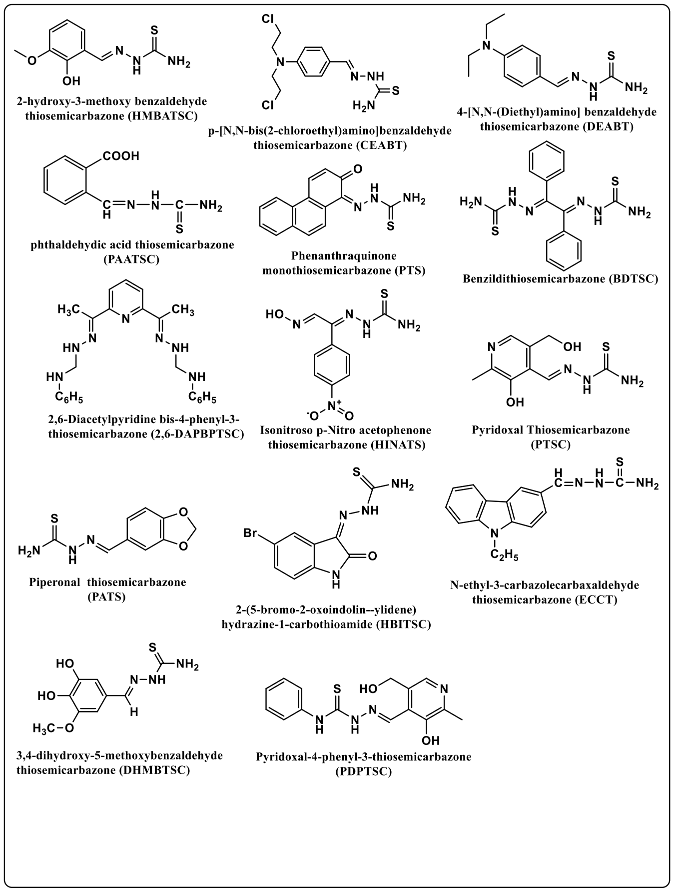

Figure 4: Thiosemicarbazone derivatives as chromogenic reagents.

2.3 Hydrazones derivatives

In inorganic chemistry, hydrazones play a critical role in building complexes with transition metal ions. These compounds include a conjugated C-N bond with a lone pair of electrons on the functional atom [90]. While the nitrogen atoms in hydrazones (Figure 5) are nucleophilic, the carbon atom behaves both electrophilic and nucleophilic. Hydrazones have special chemical and physical characteristics along with a C-N connection [91]. They can cure illnesses including TB, leprosy and mental problems while acting as models for biological species. Hydrazones serve as the versatile chemical agents, including nematocides, herbicides, insecticides, rodenticides and plant growth regulators [92]. Since hydrazones may readily form stable complexes with the majority of transition metal ions, these are useful in inorganic chemistry. Hydrazone complexes have garnered more attention with increasing growth of bioinorganic chemistry, partly because several of these complexes have been identified as potential models for biologically significant species [93]. Hydrazones have been the subject of increasing interest in research due to their anticancer, antimicrobial and antitubercular properties [94, 95]. Analytically, the hydrazone derivatives (Figure 6) help in determination of PGMs using numerous spectrophotometric procedures, briefed as under (Tables 4a -4b).

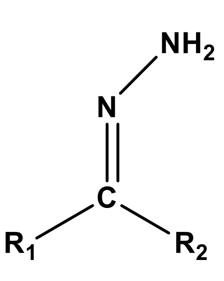

Figure 5: Hydrazones

Table 4a: Spectrophotometric Determination of PGMs using Hydrazone derivatives as Ligand

Derivative used	**Metal Detected**	**Aqueous conditions; Composition**	**Solvent; λ_{max} (nm)**	**Molar Absorptivity ($L\ mol^{-1}cm^{-1}$)**	**Comments**	**Reference**
2,4-dihydroxyl acetophenone-p-hydroxylbenzoylhydrazone (RPPHBH)	Pd (II)	Buffer, pH 5.5; 1:1	Water; 375	0.85 x 10^4	-	96
Diacetyl Monoxime Isonicotinoylhydrazone (DMIH)	Ru (II)	Buffer, pH 4.5; 1:1	Water; 346	1.4 x 10^4	-	97
3,5-Dimethoxy-4-hydroxy benzaldehydeisonicotinoylhydrazone (DMHBIH)	Ru (II)	Buffer, pH 4.5; 1:1	Water; 390	1.7 x 10^4	-	98
	Pd (II)	Buffer, pH 5.5, Triton X-100; 1:1	Water; 382	2.2 x 10^4	Cu(II), Cr(VI), Au(III) and Ru(III) seriously interfere	99
2-Aminoacetophenone isonicotinoylhydrazone (2-AAINH)	Pd (II)	Buffer, pH 4.0; 1:2	C_3H_7NO; 500	3.0 x 10^4	-	100
2,4-Dimethoxy benzaldehyde isonicotinoyl hydrazone (DMBIH)	Os (VIII)	Buffer, pH 5.0, Triton X-100; 1:2	Water; 393	1.48 x 10^4	-	101
5-Bromo salicylaldehyde Isonocotinoylhydrazone (5-BrSAINH)	Pd (II)	DMF, pH 2.5-3.0; 1:1	Water; 445	1.3 x 10^4	Fe (III) and Hg(II) interfere	102
2-Hydroxy-5-methylaceto Phenoneisonicotinoylhydrazone (HMAINH)	Pd (II)	0.01M H_2SO_4,60-90 sec. equilibration time; 1:1	$CHCl_3$; 385	0.5320 x 10^4	Shaking time of 60s to 90s required for complete extraction	103
3,4-dihydroxybenzalde-hydeisonicotinoyl Hydrazine (3,4-DHBINH)	Pd (II)	Buffer, pH 3.0; 1:1	Water; 380	0.53 x10^4	-	104
Cinnamaldehydeisonicotinoylhydrazone (CINH)	Ru (III)	Buffer, pH 3.0; 1:1	Water; 402	4.56 x 10^5	-	105
	Pd (II)	Buffer, pH 3.0-6.0; 1:1	Water; 412	1.03 x 10^4	Mo(VI), Cu(II), Th (IV) and V(V) interfere	106
3,5-Dimethoxy-4-hydroxy benzaldehydeisonicotinoylhydrazone (DMHBIH)	Pd (II)	Buffer, pH 5.5, Triton X-100; 1:1	Water; 382	2.44 x 10^4	Cu(II), Cr(VI), Au (III) and Ru (III) seriously interfere	107
	Ru(III)	Buffer, pH 4.25, Triton X-100; 1:1	Water; 390	1.7 x 10^4	V(V), Cr(VI), As (III) and Sb (III) interfere	108
4-Hydroxy-3,5-dimethoxy benzaldehyde-4- hydroxyl benzoylhydrazone (HDMBHBH)	Pd (II)	Buffer, pH 3.0, Triton X-100; 1:1	Water; 373	7.5 x 10^4	Cu(II), Fe(III) and Mo (VI) interfere	109
	Ru (VI)	5% CTAB, pH 5.5; 1:1	Water; 420	3.00 x 10^4	-	110
Cinnamaldehyde-4-hydroxybenzoyl hydrazine (CMHBH)	Pd (II)	Buffer (pH 4.0); 1:1	CH_2Cl_2; 375	6.0 x 10^4	Cu(II), Fe(III), Mo (VI) interfere	111
2-Hydroxy-1-naphthaldehyde-p-hydroxybenzoic hydrazine (HNHBH)	Pd (II)	Buffer, pH 4.0, Triton X-100; 1:1	Water; 430	2.48 x 10^4	-	112
Isonitroso-p-methyl acetophenone phenyl hydrazone (HIMAPH)	Pd (II)	1M CH_3COOH, 2M Buffer, Heating for 4-5 min. 1:2	$C_6H_5CH_3$; 470	1.3305 x 10^4	Heating on boiling water bath for 4-5 min.	113
	Rh (III)	2M Buffer, pH 5.0, Heating for 50-60min.; 1:3	$C_6H_5CH_3$; 465	2631.58	Heating on water bath 50-60 min.	114
	Ru (III)	2M Buffer, pH 4.5-5.5, Heating for 30-35min; 1:3	$C_6H_5CH_3$; 460	3535.35	Heating for 30-35min., Less sensitive	115
2-nitrobenzaldehyde thiocarbohydrazone (2-NBATCH)	Os (VIII)	0.8M HCl, 5 min. equilibration time; 1:2	$CHCl_3$; 440	8.94 x 10^3	Equilibration time 5min.	116
	Ru (III)	0.7M Aq.CH_3COOH, 5 min. heating; 1:3	$C_2H_2Cl_2$; 445	1.41 x 10^4	5 min. heating on water bath	117
	Pt (IV)	1,4-dioxane, Heating for 5min., Equilibration time of 5 min.; 1:2	$CHCl_3$; 440	1.03 x 10^4	5 min. heating in boiling water bath; Equilibration time of 5 min.	118
5-chloro-2-hydroxythio benzhydrazide (5-Cl-2-OHTBH)	Os (VIII)	HCl, Heating for 25 min., Waiting time 30min.; 1:2	$CHCl_3$; 510	1.056 x 10^4	Heating on boiling water bath for 25min.; Waiting time 30min.	119
	Ru (III)	6M HCl, Heating for 25min	$C_{10}H_8$; 535	1.516 x 10^4	Heating on boiling water bath for 25min.	120

Table 4b: Spectrophotometric Determination of PGMs using Hydrazone derivatives as Ligand

Derivative used	Metal Detected	Aqueous conditions; Composition	Solvent; λ_{max}(nm)	Molar Absorptivity ($Lmol^{-1}cm^{-1}$)	Comments	Reference
N-(o-methoxybenzaldehyde) -2-aminophenol (NOMBAP)	Rh (III)	Buffer, pH 5.5, 20-25 min. digestion time, equilibration time of 1min.; 1:3	CCl_4; 480	8248.23	20-25 min. digestion on boiling water bath, equilibration time of 1min.	121
	Ir (III)	Buffer, pH 6.5, 30 min. heating in boiling water bath, equilibration time of 1min.; 1:3	$CH_3(CH_2)_4OH$; 460	69930	30 min. heating in boiling water bath for digestion; equilibration time of 1min.	122
	Ru (III)	Buffer, pH 5.0, 15-20 min. boiling on water bath digestion time, equilibration time of 1min.; 1:3	$CHCl_3$; 490	14177.21	Digestion in boiling water bath for 10-15min.; equilibration time of 1min.	123
2-[(5-bromo-2-pyridylazo)]-5-diethylamino-phenol (5-Br-PADAP)	Pt (II)	Buffer, pH 5.0±0.2, $SnCl_2$.; 2 min. equilibration time; TX-100; 1:1:1:1	CH_2Cl_2; 575	6.0 x 10^4	Equilibration time of 2 min. required	124
	Pd (II)	Buffer, pH 3.53; 1:2	CH_2Cl_2; 585	3.86 x 10^4	Cr(VI), Fe (II) and Th (IV) interfere	125
	Ru (IV)	Buffer; equilibration time 2 min.; 1:3	CH_2Cl_2; 560	3.0 x 10^4	Equilibration time of 2 min. required	126

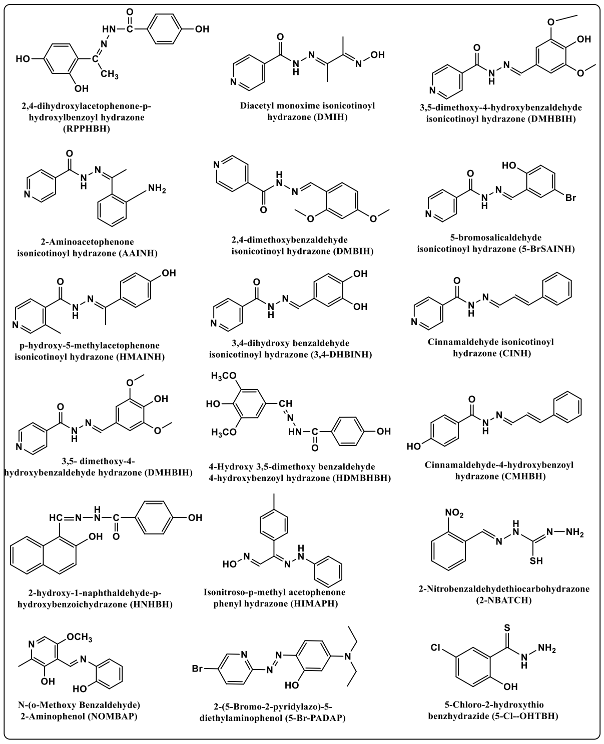

Figure 6: Hydrazones derivatives as chromogenic reagents

2.4 Miscellaneous

2.4.1 4H-1-Benzopyrans

In medicinal chemistry, benzopyrans (Figure 7) are a special kind of bicyclic heterocyclic systems. The prefix "benzo" in the name denoted a ring of benzene fused with a structure of pyran. Any heterocyclic ring containing an oxygen atom and carbons is referred to as a "pyran." Both natural and synthetic products often contain the benzopyran ring system [127]. Natural and synthetic drug building blocks are primarily composed of pyran heterocyclic compounds [128-132]. Heterocyclic compounds containing pyran were categorized according to the hydrogen atom's location and place of origin. The 4*H*-1-benzopyran derivatives find a large scope in the field of research involving material, medicinal, agriculture and biological chemistry [133]. From a survey on literature, *4H*-1-benzopyrans (Figure 8) are found to possess a good chromogenic and chelating tendency, hence proving as a versatile class of complexing agents that are used for the spectrophotometric determination of the metal ions including PGMs. The groups responsible for their analytical/chelating behaviour are the oxygen donor carbonyl and the hydroxyl groups present in their structures [127]. A till date study on the said applicability of the 4*H*-1-benzopyrans has been summarized below:

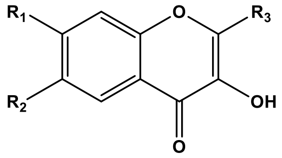

Figure 7: **Benzopyrans**

A chloroform extractable, coloured complex of 3-hydroxy-2-tolyl-*4H*-chromen-4-one (HToC) is formed with platinum in its divalent oxidation state in $NaHCO_3$ medium. The Pt (II)-HToC complex exhibited absorption maximum at 520 nm. Limit of detection and apparent molar absorptivity of the complex are 0.0147μg mL^{-1} and 6.790 x 10^4 L mol^{-1} cm^{-1}, respectively [134]. The method had been successfully used for analysis of platinum in a wide variety of analytical samples. HToC has also been successfully used to analyze iridium in trivalent state [135]. Satisfactory analysis of various synthetic samples and the radical scavenging potential of the newly developed Ir(III)-HToC complex were the practical applications of the studied method.

Complexation of platinum (II) and iridium (III) was carried out with 3–hydroxy-2-(4-methoxyphenyl)-*4H*-chromone (HMPC). Where the Pt (II)-HMPC complex [136] was produced from a 2M $NaHCO_3$ as a reaction medium and after its extraction into dichloromethane with the maximum absorption noted at 507 nm, the Ir (III)-HMPC complex [137] was formed in presence of H_3PO_4 medium in the water phase only and exhibiting a maximum absorption at 425 nm. The Pd (II)-HMPC complex showed the molar attenuation coefficient of the two complexes, respectively, was 7.1206×10^4 L mol^{-1} cm^{-1} and 6.824 x 10^4 L mol^{-1} cm^{-1}. A spectrophotometric method for detecting micro amounts of palladium in its +2 oxidation state had been developed, utilizing a new 1-benzopyran derivative. Using this method, a 1:2 complexation of palladium is made with 3-hydroxy-2-(4-methoxyphenyl)-4-oxo-*4H*-1-benzopyran resulting in 1:2 [Pd(II):HMPB] light yellow extractable complex that shows absorption maximum at 415 nm. The technique satisfied the requirements for accuracy, sensitivity and precision with a molar absorptivity of 3.011 x 10^4 L mol^{-1} cm^{-1} [138].

N. Kaur *et al.* utilized the fluid extraction technique to examine the effect of chromogenic ligand, 3-hydroxy-2-[2'-(5'-methylthienyl)]-4-oxo-4*H*-1-benzopyran (HMTB) on palladium metal in its bivalent oxidation state. With linearity up to 1.5 μg mL^{-1}, the study demonstrated optimal settings for the complexation of Pd (II)-HMTB in the stoichiometric ratio of 1:2 .This fast and accurate approach works well with a wide range of alloy samples, tailored mixes and industrial goods [139].

A non-extractable light yellow coloured complex of 3-hydroxy-2-(3′-methyl-2′-thienyl)-4-oxo-*4H*-1-benzopran (HMTB) is formed with iridium (III) in phosphoric acid medium at 415 nm. Beers's law obedience of the complex was valid up to 1.5μg mL^{-1} of Ir (III) and the apparent molar absorptivity as evaluated was 8.45 x 10^4 L mol^{-1} cm^{-1} [140]. Similarly, 6-chloro-3-hydroxy-7-methyl-2-(2'-thienyl)-4-oxo-*4H*-1-benzopyran (CHMTB) formed a yellow complex with iridium (III) in phosphoric acid medium of pH 4.63. Molar extinction coefficient of the complex was 1.18 x 10^5 L mol^{-1} cm^{-1} at 415nm [141]. Palladium in traces had been analyzed in its divalent oxidation state, spectrophotometrically using 6-chloro-3-hydroxy-7-methyl-2-(2′-thienyl)-4-oxo-4*H*-1-benzopyran (CHMTB) as a colouring agent [142]. The metal interacted with CHMTB in a ratio of 1:1 to give a dark yellow complex in $NaHCO_3$ solution ranging from 0.01-0.025 M strength.

Another benzopyran derivative, 6-chloro-3-hydroxy-7-methyl-2-(2′-furyl)-4*H*-chromen-4-one (CHMFC), helped in determining Palladium in divalent state from a basic medium provided by 0.025-0.040 M sodium bicarbonate solution and producing a 1:1 Pd(II)-CHMFC complex [143]. The method is applied effectively in Pd-charcoal catalyst, alloys, water samples and numerous synthetic mixtures.

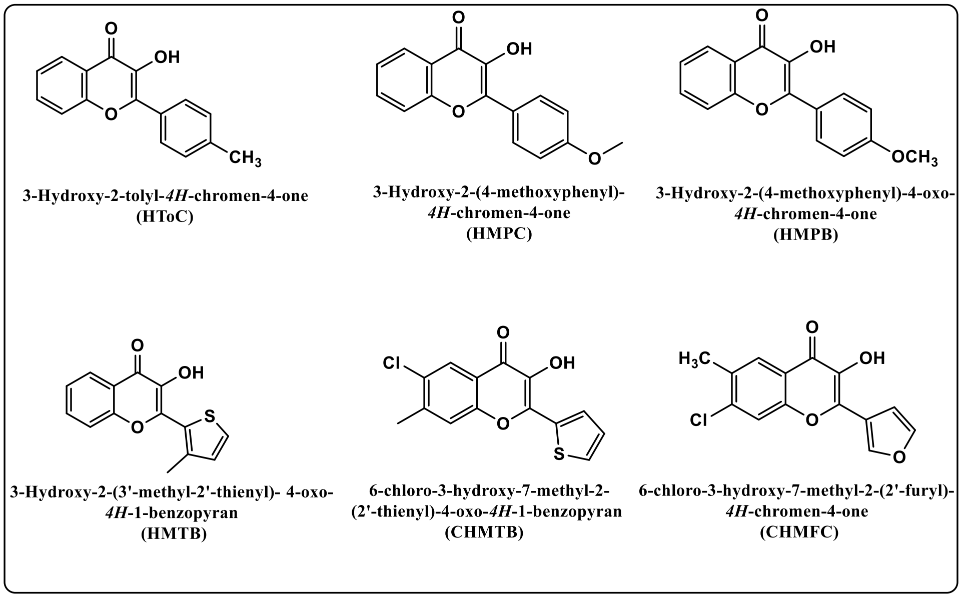

Figure 8: Benzopyran derivatives as chromogenic reagents.

2.4.2 Dyes

Colour is a popular attraction for humans and dyes are the coloured compounds that absorb electromagnetic radiations. These compounds are aromatic delocalized electron systems, responsible for absorbing varying wavelengths of radiation. Chromophores, which make energy changes in the delocalized electron cloud of a dye, make it proficient in absorbing radiation. The human eye detects this absorption and responds to colors. However, removal of electrons may cause colour loss or revert to local orbits.This results in an idea of using the dyes as chromophores in the complexation and spectrophotometric detection of the metal ions [144] especially the PGMs. The dyes that had been satisfactorily studied for the metal's analysis are shown in Figure 9.

5-[2-(4-Hydroxyphenyl)hydrazineylidene]-4-iminothiazolidine-2-one, HPIT (Figure 9), in basic medium (2M NaOH) gives coloured species with iridium (IV) which absorbs at 328 nm. The molar absorption coefficient of the complex in the aqueous phase was observed to be 5.57 x 10^3 L mol^{-1} cm^{-1} [145].

Iridium (IV) gives a coloured complex with Xylene cyanol FF (Figure 9) in the presence of 0.02 M sulphuric acid in the aqueous phase. The complexation required heating at 95˚C [146]. A non-extractable species of platinum (IV) is formed with Xylene cyanol FF in sulphuric acid medium. The complex attained maximum colour intensity only after heating at 90ºC for 30 minutes. Molar absorptivity of the complex formed was 5.1 X 10^4 L mol^{-1} cm^{-1} at 620 nm, the wavelength of maximum absorption [147].

Investigations were conducted into the Os (IV)-Orange G (Figure 9) complex formation. The reaction's ideal circumstances for the complexation were pH = 5.80 (0.20 M acetate buffer solution); 30 minutes of boiling water bath heating and two-fold reagent excess. At 540 nanometers, the effective molar absorptivity was 1.1 x 10^4 L mol^{-1} cm^{-1} [148].

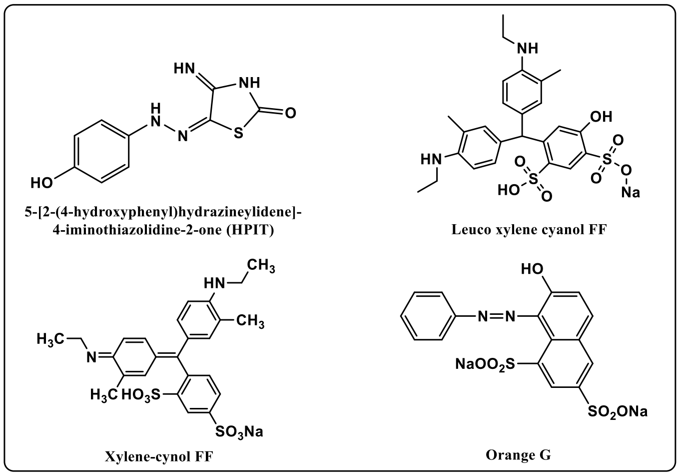
5-[2-(4-hydroxyphenyl)hydrazineylidene]-4-iminothiazolidine-2-one (HPIT)
Leuco xylene cyanol FF
Xylene-cynol FF
Orange G

Figure 9: Dyes as chromogenic reagents.

2.4.3 Thiones

Ruthenium (III) forms coloured complexes with BHMBT (Figure 10) in HCl solution with a heating of 7 minutes [149]. The complex formed is extractable in methyl isobutyl ketone (MIBK). The molar absorptivity and λ_{max} have been found to be 5.054 x 10^3 L mol^{-1} cm^{-1} and 660 nm, respectively. A coloured complex of osmium (VIII) is formed with BHMBT in 1M HCl and 1M $HClO_4$ acid solutions which can be extracted into MIBK with λ_{max} 520 nm and 540 nm, respectively. The molar absorptivity in both the cases has been found to be 4.907 x 10^4 L mol^{-1} cm^{-1} [150]. At 370 nm, BHMBT is used for the spectrophotometric determination of palladium (II) as its coloured complex in 0.7-3.5M $HClO_4$ solution. The complex is extractable into methyl isobutyl ketone and shows maximum absorption at 370 nm with molar absorptivity 1.543 x 10^4 L mol^{-1} cm^{-1} [151].

Certain triazoles are also noticed to bind to some PGMs and hence helping in their analysis. One of the triazoles, 4-(4´-fluorobenzylideneamino)-3-methyl-5-mercapto-1,2,4-triazole (FBIMMT ; Figure 10) reacts with ruthenium (III) in an acetate buffer medium to give a colored complex between the two. The complex is extractable in n-butanol with maximum absorbance measured at 394 nm. Molar absorptivity of the complex formed is 2.75 x 10^3 L mol^{-1} cm^{-1} [152]. Similarly, a 1:1 complex of palladium (II) is formed with FBIMMT at room temperature in HCl medium absorbing maximum at 390 nm. The calculated molar absorptivity of the complex is 5.404 x 10^3 L mol^{-1} cm^{-1} [153].

At pH 5.0, 1, 3-bis (hydroxymethyl) benzimidazole-2-thione (BTAHQ; Figure 10) forms a complex with iridium (III) in aqueous phase with absorbance measured at 563 nm. The apparent molar absorptivity of the complex was evaluated to be 4.81 x 10^4 and 4.26 x 10^7 L mol^{-1} cm^{-1} [154].

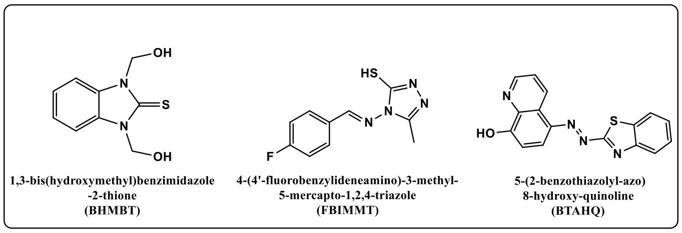
1,3-bis(hydroxymethyl)benzimidazole -2-thione (BHMBT)
4-(4'-fluorobenzylideneamino)-3-methyl-5-mercapto-1,2,4-triazole (FBIMMT)
5-(2-benzothiazolyl-azo) 8-hydroxy-quinoline (BTAHQ)

Figure 10: Thione derivatives as chromogenic reagents

CONCLUSION

The remarkable chemical stability of platinum group metals (PGMs) under diverse environmental conditions and high temperatures makes them indispensable in the fields of chemical engineering and chemistry. Across a wide range of industries, their distinctive qualities make them extremely valuable material. However, as PGM reserves gradually disappear, recycling waste that contains PGMs is imperative in order to guarantee the prudent use of available resources. When it comes to obtaining these metals, recycling catalytic waste, as opposed to the traditional method of mining from natural ores, offers a more economical and environmentally responsible choice. Recent research indicates that the platinum, palladium, and rhodium group metals (PGMs) that are emitted from car catalytic converters are accumulating beside roadsides. Concerns regarding the toxicity of PGMs to living things and their effects on the environment are being raised by the rising concentrations of PGMs in the environment as a result of this deposition. The growing interest in the medicinal inorganic chemistry, based upon the use of metal complexes especially the PGM complexes as drugs, has led to the detection of metal ions in trace quantities. This review flourishes the arena of spectrophotometric determination of metal ions in their complexes. UV/VIS spectrophotometric technique is having a great demand in wide array of sectors, even though it is regarded as obsolete by the analysts. The fact behind this is the better detection limit and selectivity of the atomic absorption spectrophotometry and the inductively coupled emission spectroscopy along with the mass spectrophotometry. However, still UV-VIS spectrophotometry is well known and used due to its advantages of being inexpensive, easy availability, comparable sensitivity, selectivity and more commonly the accuracy and precision. Advances on the synthesis of different reagents have led the scope for the researchers to work with these techniques for the determination of trace metal ions. The sensitivity and utility of the complexes can be improved using different complexing reagents. Thus, this technique can be regarded as a competitive technique for the detection of metals in atleast trace amounts.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

REFERENCES

1. C.R.M. Rao, G.S. Reddi. Platinum group metals (PGMs); occurrence, use and recent trends in their determination. *Trends in Analytical Chemistry*, **2000**, 19(9), 565-586. https://doi.org/10.1016/S0165-9936(00)00031-5
2. H. Renne, G. Schlamp, I. Kleinwächter, E. Drost, H.M. Lüschow, P. Tews, P. Panster, M. Diehl, J. Lang, T. Kreuzer, A. Knodler, K.A. Starz, K. Dermann, J. Rothaut, R. Drieselmann, C. Peter, R. Schiele, J. Coombes, M. Hosford, D.F. Lupton. Platinum Group Metals and Compounds. *Ullmann's Encyclopedia of Industrial Chemistry*, **2018,** 28**,** 1-73. http://dx.doi.org/10.1002/9783527306732.a21_075.pub2
3. A.S. Darling. Some Properties and Applications of the Platinum-Group Metals. *International Metallurgical Reviews,* **1973**, 18(3), 91–122. https://doi.org/10.1179/imtlr.1973.18.3.91
4. H.E. Hilliard. Platinum Recycling in United States in 1988, *U.S. Geological Survey: Reston, VA, USA*, **2001**. https://doi.org/10.3133/cir1196B
5. A. Markowska, B. Kasprzak, K. Jaszczyńska-Nowinka, J. Lubin, J. Markowska. Noble metals in oncology. *Współczesna Onkologia,* **2015,** 19(4), 271-275. https://doi.org/10.5114/wo.2015.54386
6. J. Ohata, Z.T. Ball. Rhodium at the chemistry-biology interface, *Dalton Transactions*, **2018**, 42, 14855-14860. https://doi.org/10.1039/C8DT03032D
7. B M Anthony. "9. Platinum group metals". *Metals and Alloys: Industrial Applications*, Berlin, Boston: De Gruyter, **2016**, 55-64. https://doi.org/10.1515/9783110441857-010
8. A.E. Hughes, N. Haque, S.A. Northey, S. Giddey. Platinum Group Metals: A Review of Resources, Production and Usage with a focus on Catalysts. *Resources*, **2021**, 10(9),93. https://doi.org/10.3390/resources10090093
9. S. Rauch, B. Peucker-Ehrenbrink.Sources of Platinum Group Elements in the Environment, *Platinum Metals in the Environment*, **2014**, 3-17. https://doi.org/10.1007/978-3-662-44559-4_1
10. J.E. Mungall, A.J. Naldrett. Ore deposits of the Platinum-Group Elements, *Elements*, **2008**, 4(4), 253-258. https://doi.org/10.2113/gselements.4.4.253
11. F. Habashi. Two hundred years platinum group metals, *Metall*, **2003**, 57(12), 798-805.
12. M A Benvenuto. Metals and Alloys (Industrial Applications) || 9. Platinum group metals. , *De Gruyter*, **2016**, 55-63. https://doi.org/10.1515/9783110441857-010

13. K. Pianowska, J. Kluczka, G. Benke, K. Goc, J. Malarz, M. Ochmański, K. Leszczyńska-Sejda. Solvent Extraction as a Method of Recovery and Separation of Platinum Group Metals, *Materials*, **2023**, 16(13), 4681. https://doi.org/10.3390/mal16134681
14. F.R. Hartley, (Ed.). Chemistry of the platinum group metals: recent developments, *Studies in Inorganic Chemistry*, **1991**, 11, 2-642.
15. R. J. Seymour, J.O´Farrelly. Kirk-Othmer Encyclopedia of Chemical Technology || *Platinum-Group Metals*, **2012**. https://doi.org/10.1002/0471238961.1612012019052513
16. D. Givan. Precious Metals in Dentistry, *Dental Clinics of North America*, **2007**, 51(3), 591-601. https://doi.org/10.1016/j.cden.2007.03.005
17. J. Groothuis, N.F. Ramsey, G. M. J. Ramakers, G. van der Plasse. Physiological Challenges for Intracortical Electrodes, *Brain Stimulation*, **2014**, 7(1), 1-6. https://doi.org/10.1016/j.brs.2013.07.001
18. B.K. Woodward. Platinum group metals (PGMs) for permanent implantable electronic devices, *Precious Metals for Biomedical Applications*, **2014**, 130-147. https://doi.org/10.1533/9780857099051.2.130
19. A. Cowley, B. Woodward. A Healthy Future: Platinum in Medical Applications, *Platinum Metals Reviews*, **2011**, 55(2), 98-107. https://doi.org/10.1595/147106711X566816
20. Y. Bai, G. Aodeng, L. Ga, W. Hai, J. Ai. Research Progress of Metal Anticancer Drugs, *Pharmaceutics*, **2023**, 15(12), 2750. https://doi.org/10.3390/pharmaceutics15122750
21. C. Zhang, C. Xu, X. Gao, Q. Yao. Platinum-based drugs for cancer therapy and anti-tumor strategies, *Theranostics*, **2022**, 12(5), 2115-2132. https://doi.org/10.7150/thno.69424
22. A.T. Odularu, P.A. Ajibade, J.Z. Mbese, O.O Oyedeji. Developments in Platinum-Group Metals as Dual Antibacterial and Anticancer Agents, *Journal of Chemistry*, **2019**, 5459461(1-18). https://doi.org/10.1155/2019/5459461
23. Z. Marczenko, H. Freiser. Spectrophotometric Determination of Trace Elements, *C R C Reviews in Analytical Chemistry*, **1981**, 11(3), 195-260. https://doi.org/10.1080/10408348108542732
24. T.F. Vasekina, I.V. Boryagina, E.S. Pyatakhina, N.V. Rovinskay. Specific features of gravimetric determination of palladium in palladium containing objects. *Inorganic Materials Applied Research*, **2014**, 50, 1371-1374. https://doi.org/10.1134/S0020168514140143
25. T.M. Malyutina, B.V. Shneider, T.Y. Alekseeva, Y.A. Karpov. Determination of high concentrations of palladium by combined use of gravimetric and spectral analysis, *Inorganic Materials Applied Research*, **2013**, 49(14), 1277-1282. https://doi.org/10.1134/S0020168513140070
26. G.A. Ottewill, B.A. Plunkett, F.C. Walsh. The Analysis of Metal Ions in Solution. *Transactions of the IMF*, **1993**, 166-170. https://doi.org/10.1080/00202967.1993.11871012
27. A. Shams, N. Ashraf, M.H. Arbab Zavar, M. Masrournia. Electrochemical generation of palladium volatile species enhanced with Sn(II): application for detection of Pd(II) by pyrolytic graphite coated furnace atomic absorption spectrometry, *Journal of Analytical Atomic Spectrometry*, **2019**, 5, 963-971. https://doi.org/10.1039/C8JA00406D
28. X. Jia . Determination of palladium by graphite furnace atomic absorption spectroscopy without matrix matching, *Talanta*, **2001**, 54(4), 54(4), 741-751. http://dx.doi.org/10.1016/S0039-9140(01)00324-1
29. N.S. Marinkovic, K. Sasaki, R.R. Adzic. Determination of Single- and Multi-Component Nanoparticle Sizes by X-ray Absorption Spectroscopy, *Journal of Electrochemical Society*, **2018**, 165(15), J3222-J3230. https://doi.org/10.1149/2.0281815jes
30. J.E. Jaine, M.R. Mucalo. Rapid determination of rhodium, palladium, and platinum in supported metal catalysts using multivariate analysis of laser induced breakdown spectroscopy data, *Spectrochimica Acta*, **2018**, 145, 58-63. https://doi.org/10.1016/j.sab.2018.04.009
31. D.D. Das, N. Sharma, P.A. Chawla. Neutron Activation Analysis: An Excellent Nondestructive Analytical Technique for Trace Metal Analysis, *Critical reviews in Analytical Chemistry*, **2023**, 1-17. https://doi.org/10.1080/10408347.2023.2178841
32. J.C.B Richard, M.J.T Milton. Analytical techniques for trace element analysis: an overview, *Trends in Analytical Chemistry*, **2005**, 24(3), 266-274. https://doi.org/10.1016/j.trac.2004.11.010
33. K. Liu, X.Gao, L. Li, C.-T. A., Chen, Q. Xing. Determination of ultra-trace Pt, Pd and Rh in seawater using an off-line pre-concentration method and inductively coupled plasma mass spectrometry, *Chemosphere*, **2018**, 212, 429-437. https://doi.org/10.1016/j.chemosphere.2018.08.098
34. Y. Yildiz, M. Kotb, A. Hussein, M. Sayedahmed, M. Rachid, M. Cheema. Determination of Palladium II in 5% Pd/BaSO$_4$ by ICP-MS with Microwave Digestion, and UV-VIS Spectrophotometer, *American Journal of Chemistry*, **2019**, 10(4), 127-136. https://doi.org/10.4236/ajac.2019.104011
35. M.Y. Burylin, A.A. Pupyshev. Development of electrothermal atomic absorption spectrometry in 2005-2016, *Journal of Analytical Chemistry*, **2017**, 72, 935-946. https://doi.org//10.1134/S1061934817090039
36. M. Picollo, M. Aceto, T.Vitorino. UV-VIS spectroscopy, *Physical Sciences Reviews*, **2019**, 1-14. https://doi.org/10.1515/psr-2018-000
37. E. Bulska, A. Ruszczyńska. Analytical Techniques for Trace Element Determination, *Physical Sciences Reviews,* **2017**, 2(5). http://doi.org/10.1515/psr-2017-8002
38. N. Kaur, N. Agnihotri, R. Agnihotri, R.K. Sharma. A Treatise on Spectrophotometric Determination Techniques of Palladium(II) Ions, *Journal of Chemical Reviews*, **2022**, 4(2), 81-99. https://doi.org/10.22034/jcr.2022.325620.1139
39. M. Muhammad, S. Khan, S.A. Shehzadi , Z. Gul , H.M. Al-Saidi , A. W. Kamran , F. A. Alhumaydhi. Recent advances in colorimetric and fluorescent chemosensors based on thiourea derivatives for metallic cations: A review. *Dyes and Pigments*, **2022**, 205(9), 110477. http://dx.doi.org/10.1016/j.dyepig.2022.110477
40. B. Joseph, S. John, M. Prajila, A. Joseph. Spectrophotometric determination of osmium (VIII) in trace amounts using ethylene Thiourea (ETU) as chromogenic reagent, *Indian Journal of Chemical Technology*, **2011**, 113-117.
41. G. Bratulescu, G. Ion, G. Anca. Thiocyanatochrome complexes in analytical chemistry. Determination of osmium(III), *Journal of the Serbian Chemical Society*, **2005**, 1113-1119. http://dx.doi.org/10.2298/JSC0509113B
42. K.S. Patel, P.C. Sharma, S.G. Aggarwal, P. Hoffmann. Specific Spectrophotometric Determination of Palladium with *N, N*′-Diphenylbenzimidoylthiourea, *Analytical Letters*, **2000**, 33(3), 503-511.
43. M. Dong-Lan, L. Ying, L. Quan-Jian, W. Yu-Lu. Spectrophotometric Determination of Palladium(II) with New Reagent N-octyl-N´-(sodium-p-amminobenzenesulphonate thiourea), *Journal of the Chinese Chemical Society,* **2001**, 48, 1111-1114.
44. X. Zhang , Y. Zhou, H. Zhangjie, H. Qiufen, C. Jing , Y. Guangyu, X. Zhang, Y. Zhou, H. Zhangjie, H. Qiufen , C. Jing , Y. Guangyu, Study of Solid Phase Extraction Prior to Spectrophotometric Determination of Platinum with N-(3,5-Dimethylphenyl)-N´-(4-Aminobenzenesulfonate)-Thiourea, *Microchimica Acta*, **2006**, 153, 187-191.
45. L. Zhigang , L. Xuemei, Z. Liya, Hu. Qiufen, C. Jing, Y. Guangyu. Solid phase extraction and spectrophotometric determination of platinum (IV) with N-(3,5-Dimethylphenyl)-N´-(4-Aminobenzenesulfonate)-Thiourea, *Indian Journal of Chemistry*, **2006**, 45A, 1852-1855.
46. D. Ma, F. Cui, D. Xia, Y. Wang. Spectrophotometric Determination of Copper and Palladium using a new reagent, *Analytical Letters*, **2001**, 35(2), 413–421. https://doi.org/10.1081/AL-120002539
47. D. Ma, Y. Li, K. Ma, J. Li, J. Chen, Y. Wang. A high-selectivity spectrophotometric reagent for determining platinum (IV), *Talanta*, **2001**, 53(5), 937-941. https://doi.org/10.1016/s0039-9140(00)00583-x
48. Y. S. Shelar , H. R. Aher , S.R. Kuchekar, S. H. Han. Extractive spectrophotometric determination of palladium(II) with o-methyl phenyl thiourea from synthetic mixtures, *Bulgarian Chemical Communications*,**2011**, 45(2), 172-179.
49. S.R. Kuchekar, Y.S. Shelar, S-H. Han. Spectrophotometric determination of platinum (IV) through the O-methylphenyl thiourea and iodide ternary complex after liquid-liquid extraction, *Brazilian Journal of Analytical Chemistry*, **2012**, 3(10), 421-428.
50. S.R. Kuchekar, Y.S. Shelar, H.R. Aher, S.H. Han. Development of a reliable analytical method for extraction spectrophotometric determination of ruthenium (III) from catalyst and fissium alloy using o-methylphenylthiourea as a chromogenic chelating ligand, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **2013**, 106, 1–11. https://doi.org/10.1016/j.saa.2012.12.075
51. S. Kuchekar, P. Bermejo-Barrera, Y. Shelar. Rapid and selective determination of osmium (IV) by UV-visible spectrophotometry using o -methylphenylthiourea as a chromogenic chelating ligand: sequential separation

of osmium (IV), rhodium (III) and platinum (IV). *International Journal of Environmental Analytical Chemistry*, **2014**, 94(5), 463–478. https://doi.org/10.1080/03067319.2013.879294

52. Y.S. Shelar, S.R. Kuchekar, S.H. Han. Extraction spectrophotometric determination of rhodium (III) with o-methylphenylthiourea. *Journal of Saudi Chemistry Society*, **2015**, 19, 616-627. https://doi.org/10.1016/j.jscs.2012.04.013
53. S.R. Kuchekar, S.D. Pulate, Y.S. Shelar, S.H. Han. Spectrophotometric study of interaction of *o*-methylphenyl thiourea with iridium(III) and development of a precise determination method from hydrochloric acid media, *Indian Journal of Chemical Technology*, **2014**, 21(2), 120-126.
54. S. Kuchekar, R. Navalb, S.-H. Hanc. Development of a Reliable Method for the Spectrophotometric Determination of Palladium (II) with o-Methoxyphenyl Thiourea : Separation of Palladium from Associated Metal Ions, *South African Journal of Chemical Engineering*, **2014**, 67, 226–232.
55. S.R. Kuchekar, Y.S. Shelar, R.J. Bhor, M.A. Anuse, R.M. Naval. Separation and Spectrophotometric Determination of Osmium (IV) and Ruthenium (III) with *O*-methoxyphenyl Thiourea as Chromogenic Ligand: Sequential Separation of Osmium (IV), ruthenium (III), and Platinum (IV).*Separation Science and Technology*, **2015**, 50(8), 1190-1201. https://doi.org/10.1080.01496395.2014.983245
56. D. Ma, G. Ding, J. Wang. Simultaneous determination of gold (III), palladium (II), and platinum (IV) with *N*-phenyl-*N′*-(sodium p-aminobenzenesulfonate) thiourea. *Analytical and Bioanalytical Chemistry*, **2002**, 372(5-6), 740–743. https:/doi.org/10.1007/s00216-001-1219-1
57. S.R. Kuchekar, H.R. Aher, S.D. Bhumkar, P. Ramasami. Solvent extraction separation and spectrophotometric determination of ruthenium (III) with p-methylphenyl thiourea: sequential separation of ruthenium, osmium and iron. *Separation Science and Technology,* **2019**, *55(4),* 1–13. https://doi.org/10.1080/01496395.2019.163562
58. S.R. Kuchekar, S. Bhumkar, H. Aher, S.-H. Han. Solvent Extraction, spectrophotometric determination of Iridium (III) using p-methylpheylthiourea as a chelating agent: Sequential Separation of Iridium (III), Ruthenium (III) and Platinum (IV), *Journal of Materials and Environmental Sciences*, **2019**, 10(12), 1200-1213.
59. S.R. Kuchekar, S.D. Bhumkar, H.R. Aher. Extractive Spectrophotometric Determination of Osmium (VIII) using pmethylphenylthiourea as a Chromogenic reagent: Mutual separation of Palladium, Osmium and Platinum*, Journal of Materials and Environmental Science*, **2019**, 10(4), 316-327.
60. S. R. Kuchekar, S. D. Bhumkar, H. R. Aher, S.H. Han. Separation of Platinum(IV) from Pharmaceuticals using p-methylphenyl Thiourea by Solvent Extraction: Separation from Palladium(II), Nickel (II), *Analytical Chemistry Letters*, **2019**, 9(6), 775-788. https://doi.org/10.1080/22297928.2020.1712236
61. S. R. Kuchekar, S.D. Bhumkar, H. R. Aher, B. H. Zaware, P. Ramasami. Solvent Extraction and Spectrophotometric Determination of Palladium(II) Using p- methylphenyl Thiourea as a Complexing Agent, *International Journal of Chemical and Molecular Engineering*, **2019**, 13(10).
62. J.S. Casas, M.S. García-Tasende, J. Sordo. Main group metal complexes of semicarbazonesandthiosemicarbazones. A structural review. *Coordination Chemistry Reviews*, **2000**, 209(1), 197-261. https://doi.org/10.1016/S0010-8545(00)00363-5
63. H. Ajudiya, M.C. Shah. Thiosemicarbazones are Good Spectrophotometric Reagent for Transition Metal Determination: A Review, *YMER*, **2022**, 152-175.
64. S. Mukherjee. Role of Thiosemicarbazide and its Derivatives as N, S Donor Ligand. *The Beats of Natural Sciences*, **2016**, 3, 1-10.
65. I.D. Kostas, B.R. Steele. Thiosemicarbazone Complexes of Transition Metals as Catalysts for Cross-Coupling Reactions. *Catalysts*, **2020**, 10(10), 1107. https://doi.org/10.3390/catal10101107
66. J. Karthikeyan, P. Parameshwara, A. N. Shetty. Analytical properties of p-[N, N-bis (2-chloroethyl)amino]benzaldehydethiosemicarbazone: spectrophotometric determination of palladium(II) in alloys, catalysts, and complexes. *Environmental Monitoring and Assessment*, **2010**, 173(1-4), 569–577. http://dx.doi.org/10.1007/s10661-010-1405-8
67. P.P. Naik, J. Karthikeyan, A. N. Shetty. Spectrophotometric determination of platinum (IV) in alloys, complexes, environmental, and pharmaceutical samples using 4-[*N, N*-(diethyl)amino] benzaldehyde thiosemicarbazone, *Environmental Monitoring and Assessment*, **2010**, 171(1-4), 639-649. https://doi.org/s10661-010-1308-8
68. F. Salinas, A. Espinosa-Mansilla, L. Lòpez-Martínez, P.L. Lòpez-de-Alba. Selective Extraction-Spectrophotometric Determination of Microamounts of Palladium in Catalysts, *Chemica Analityczna*, **2001**, 46(2), 239-248.
69. B.K. Reddy, K.J. Reddy, J.R. Kumar, A.K. Kumar, A.V. Reddy. Highly sensitive Extractive Spectrophotometric Determination of Palladium (II) in Synthetic Mixtures and Hydrogenation Catalysts Using Benzildithiosemicarbazone, *Analytical Sciences*, **2004**, 20, 925-930.
70. A.R. Somala. Synthesis of novel analytical reagent 2, 6-diacetyl-pyri-dine bis-4-phenyl-3-thiosemicarbazone and its analytical applications: Determination of Pd (II) in Spiked samples, *Journal of Chemical and Pharmaceutical Research,* **2015**, 7(8), 146-154.
71. V.D. Barhate, P. Madan, A. Kumar, S. Gupta, D. B. Mandhare. Extractive spectrophotometric determination of palladium (II) with isonitroso-p-thiosemicarbazone (HINATS), *Oriental Journal of Chemistry*, **2009**, 25(3), 731-733.
72. D.M. Renuka , M. O. Reddy. Non-Extractive Spectrophotometric Determination of Palladium in Biological Samples Using Pyridoxal Thiosemicarbazone (PTSC), *International Journal of Advanced Engineering, Management and Science*, **2017**, 3(4). https://dx.doi.org/10.24001/ijaems.3.4.19
73. K.J. Reddy, J. R. Kumar, C. Ramachandraiah , S. A. Reddy, A. V. Reddy. Selective and sensitive extractive spectrophotometric determination of micro amounts of palladium (II) in spiked samples: using a new reagent N-ethyl-3-carbazolecarbaxaledehydethiosemicarbazone, *Environmental Monitoring Assessment*, **2008**, 136, 337–346.
74. P. Madhusudhan, M. R. Reddy, J. Renuka. Spectrophotometric Determination of Ruthenium (III) with complexing with a new & freshly prepared chromogenic organic reagent 3,4- dihydroxy-5-methoxybenzaldehyde thiosemicarbazone*, International Journal of Advanced Research in Engineering and Technology*, **2021**, 12(2), 568-573. https://doi.org/10.34218/IJARET.12.2.2021.054
75. P.P. Sinha, S.K.S. Tomer, A. Asthana. Spectrophotometric Determination of Ruthenium present in traces. *International Journal of Research in Engineering and Technology*, **2015**, 1-3.
76. P.P. Sinha, S.K.S. Tomer. Spectrophotometric Determination of Rhodium using Phenanthraquinone monothiosemicarbazone, *International Journal of Technical Research and Applications*, **2017**, 42, 05-06.
77. P.P. Sinha, A. Mishra, S.K.S. Tomar. Spectrophotometric Determination of Osmium, *Global Journal of Engineering Science and Researches*, **2019,** 61-63.
78. P. Madan, V. Barhate. Extractive Spectrophotometric Determination of Ruthenium(III) Using 2-(5-Bromo-2-Oxoindolin-3-Ylidene) Hydrazine Carbothioamide as an Analytical reagent, *International Journal of Science and Research*, **2013**, 5(4), 778-781.
79. M. Parinita, V.D. Barhate. Extractive and spectrophotometric determination of palladium (II) using 2-(5-Bromo-2-Oxoindolin-3-Ylidene) Hydrazine Carbothioamide as an analytical reagent, *Journal of Chemical and Pharmaceutical Research*, **2015,** 7(12), 1113-1116.
80. P.U. Madan, V.D. Barhate. Extractive Spectrophotometric Determination of Osmium(IV) Using 2-(5-Bromo-2-Oxoindolin-3-Ylidene) Hydrazine Carbothioamide as an Analytical reagent, *Journal of Applicable Chemistry*, **2016**, 5(3), 646-653.
81. S.S. Borgave, V.D. Barhate. Extractive Spectrophotometric Determination of Rhodium(III) Using 2-(5-Bromo-2-Oxoindolin-3-Ylidene) Hydrazine Carbothioamide as an Analytical reagent,*EJPMR*, **2016**,475-478.
82. V.D. Barhate, P.U. Madan. Extractive Spectrophotometric Determination of Platinum(IV) Using 2-(5-Bromo-2-Oxoindolin-3-Ylidene) Hydrazine Carbothioamide as an Analytical reagent, *World Journal of Pharmacy and Pharmaceutical Sciences*, **2016**, 5(4), 1939-1947. https://doi.org/10.20959/wjpps20164-6543
83. S.S. Borgave, V.D. Barhate. Extractive Spectrophotometric Determination of Iridium(III) Using 2-(5-Bromo-2-Oxoindolin-3-Ylidene) Hydrazine Carbothioamide as an Analytical reagent, *Journal of Chemical and Pharmaceutical Research*, **2016**, 8(5), 584-589.
84. A.P. Kumar, P.R. Reddy, V.K. Reddy. Direct and Derivative Spectrophotometric determination of Ruthenium (III), *International Journal of Chem Tech Research*, **2013**, 5(4), 1442-1447.

85. I. Srivani, A.P Kumar, P.V. Reddy, K.P.P.R.M. Reddy, V.K. Reddy. Synthesis of 2-hydroxy-3-methoxy Benzaldehyde thiosemicarbazone (HMBATSC) and its application for direct and second derivative spectrophotometric determination of palladium(II), *Annali Di Chimica*, **2007**, 97(11-12), 1237-1245. https://doi.org/10.1002/adic.200790109

86. P. Shetty, A.N. Shetty, R.V. Gadag. Spectrophotometric determination of palladium (II) using piperonal thiosemicarbazone, *Indian Journal of Chemical Technology*, **2003**, 10, 287-290.

87. P. Shetty, A.N. Shetty, R.V. Gadag. Rapid spectrophotometric determination of platinum (IV) using piperonal thiosemicarbazone, *Indian Journal of Chemistry*, **2002**, 41A, 988-990.

88. L.S. Sarma, J.R. Kumar, K.J. Reddy, A.K. Kumar, A.V. Reddy. A Rapid and Sensitive Extractive Spectrophotometric determination of Palladium(II) in Synthetic Mixtures and Hydrogenation Catalysts Using Pyridoxal -4-phenyl-3-thiosemicarbazone, *Analytical Sciences*, **2002**, 18(11), 1257-1261. https://10.2116/analsci.18.1257.

89. FM. Khokhar, T.M. Jahangir, M.Y. Khuhawar, M.S. Qureshi, M.I. Khaskheli, L.A. Khan Khokhar. High Performance liquid chromatographic separation of platinum(II), gold(III), vanadium(IV), vanadium(V), molybdenum(VI) and analysis of cisplatin as platinum(II) in cis-plasol injection, urine, and blood serum using pyridoxal-4-phenyl-3-thiosemicarbazoneas complexing agent, *Journal of Liquid Chromatography & Related Technologies*, **2019**, 43(1-2), 29-36. https://doi.org/10.1080/10826076.2019.1645029

90. E. Corey, D. Enders. Applications of *N,N*-dimethylhydrazones to synthesis. Use in efficient, positional and stereochemically selective C=C and formation, oxidative hydrolysis of carbonyl compounds. *Tetrahedron Letters*, **1976**, 17(1), 3-6. https://doi.org/10.1016/S0040-4039%2800%2971307-4

91. A.J.M. Xavier, M. Thakur, J.M. Marie. Synthesis and spectral characterization of hydrazine based 14-membered octaaza macrocyclic Ni (II) complexes. *Journal of Chemical and Pharmaceutical Research*, **2012**, 4)2), 986-90.

92. R.E.D. Clark. The colorimetric determination of tiny means of Toluene-3:4-dithiol (Dithiol), *Analyst*, **1937**, 661. https://doi.org/10.1039/AN9376200661

93. C. Jayabalakrishnane, K. Natarajan. Synthesis, characterization and biological activities off Ruthenium (II) carbonyl complexes containing bifunctional tridentate Schiff bases. *Synthesis and Reactivity in Inorganic and Metal organic chemistry*, **2001**, 31(6), 983-995. http://doi.org/10.1081/SIM-100105255

94. M Katyal. Analytical applications of hydrazones. *Talanta*, **1975**, 22(2), 151-166. https://doi.org/10.1016/0039-9140(75)80161-5

95. R.B.Singh, P.Jain, R.P.Singh. Hydrazones as analytical Reagents: A Review *Talanta*, **1982**, 29(2), 77-84. https://doi.org/10.1016/0039-9140(82)80024-6

96. M. Challa, T.S. Reddy. Simple and simultaneous spectrophotometric determination of Pd(II) in alloys using hydrazone compounds, *African Journal of Pure and Applied Chemistry*, **2011**, 5(13), 442-447. https://doi.org/10.5897/AJPAC.9000126

97. M.M. Patel, M.C. Shah. Review on Spectrophotometric Method for formation of Metal Complexes of Hydrazone Derivatives, *YMER,* **2022**, 2942-2964.

98. G.C. Reddy, N. Devanna and K.B. Chandrasekhar, "Sensitive Spectrophotometric Determination of Ruthenium (III) using Diacetyl Monoxime Isonicotinoyl Hydrazone (DMIH)", *Asian Journal of Research in Chemistry*, **2011**, 4(6), 997-1000.

99. M.R. Rao, K.B. Chandrasekhar. Sensitive Derivative Spectrophotometric Determination of Palladium (II) using 3,5-Dimethoxy-4-hydroxybenzaldehydeisonicotinoylhydrazone in the presence of Micellar medium , *Der Pharma Chemica*, **2011**,3(2), 358-369.

100. M. Gangadharappa, P. R. Reddy. Direct and derivative spectrophotometric determination of palladium with 2-aminoacetophenone isonicotinoyl hydrazone (2-AAINH), *Journal of Indian Chemical Society*, **2006**, 83, 1130-1134.

101. K.A. Bai, K.B. Chandrasekhar. Spectrophotometric Determination of Osmium (VIII) using 2,4-Dimethoxy Benzaldehyde IsonicotinoylHydrazone (DMBIH) in presence of Surfactant Triton X-100, *Research Journal of Pharmaceutical, Biological and Chemical Sciences*, **2011**, 2(3), 174-182.

102. M. Swetha, P.R. Reddy, V.K. Reddy. Direct, derivative spectrophotometric determination of micro amounts of palladium (II) by 5-bromo-salicylaldehyde isonocotinoyl hydrazine (5-BrSAINH), *Advances in Applied Science Research*, **2013**, 4(2), 298-304.

103. G. B. Pethe, S. G. Bhadange, M. D. Joshi, A. S. Aswar. Extractive Spectrophotometric Determination of Palladium (ii) with 2-hydroxy-5-methyl acetophenone Isonicotinoyl hydrazone (HMAINH), *Advances in Applied Science Research*, **2010**, 1(2), 58-64.

104. S. L. Narayana, C. Ramachandraiah, A.V. Reddy, D. Lee, J. Shim. Determination of traces of Pd(II) spiked samples by using 3,4-Dihydroxybenzaldehydeisonicotinoylhydrazone as a Chelating Agent with UV Visible Spectrophotometer, *E-Journal of Chemistry*, **2011**, 8(1), 217-225.

105. V.K. Kumar, M.R. Rao, K.B. Chandrasekhar, N. Devanna. Derivative Spectrophotometric Determination of Ruthenium (III) using cinnamaldehydeisonicotinoylhydrazone reagent (CINH), *Asian Journal of Chemistry*, **2008**, 20(3), 2197-2204.

106. S.R.K. Reddy, M.R. Rao, N. Devanna, K.B. Chandrasekhar.Determination of Palladium (II) Using Cinnamaldehyde Isonicotinoyl Hydrazone by Derivative Spectrophotometric Technique, *Journal of Applicable Chemistry*, **2016**, 5(2), 375-383.

107. M.R. Rao, K.B. Chandrasekhar. Sensitive Derivative Spectrophotometric Determination of Palladium (II) using 3,5-Dimethoxy-4-hydroxybenzaldehydeisonicotinoylhydrazone in presence of Micellar medium, *Der Pharma Chemica*, **2011**, 3(2), 358-369

108. M.R Rao, K.B. Chandrasekhar, N. Devanna. Determination of Ruthenium (III) in the presence of micellar medium by derivative spectrophotometric technique*, Journal of Chemical Technology and Metallurgy Alloys 5*, **2012**, 5(1/2), 42-49. http://dx.doi.org/10.30970/cma5.0207

109. D.G. Krishna, N. Devanna, K.B. Chadrasekhar. Direct and Derivative Spectrophotometric determination of Palladium (II) in the presence of Micellar Medium in the Hydrogenation Catalyst Samples, synthetic alloys samples and in water samples using 4-hydroxy-3,5-dimethoxy Benzaldehyde 4-Hydroxy Benzoylhydrazone (HDMBHBH), *International Journal of Applied Biology and Pharmaceutical Technology*, **2010**, 1(2), 643-659.

110. D.G. Krishna, G.V. K. Mohan. Synthesis, Structural Characterization and Spectrophotometric determination of ruthenium(VI) in Presence of Micellar Medium using 4-hydroxy-3,5-dimethoxy Benzaldehyde 4-Hydroxy Benzoylhydrazone, *Engineering*, **2013**, 245-246. https://dx.doi.org/10.36106/ijar

111. D.G. Krishna, N. Devanna, K.B. Chadrasekhar. Comparative Study of Palladium(II), using 4-hydroxy 3,5-dimethoxy Benzaldehyde 4-hydroxyl benzoyl hydrazine and 4-hydroxy benzoylhydrazone in the presence of micellar medium by spectrophotometry, *International Journal of Pharma Sciences and Research*, **2010**, 1(18), 301-311.

112. P.G. Chowdary, V.S. Basha. Synthesis of 2-hydroxy-1-naphthaldehyde-p-hydroxybenzoichydrazone (HNHBH) and its applications in direct and derivative spectrophotometric determination of palladium (II), *World Journal of Pharmaceutical Research*, **2015**, 4(5), 1168-1180.

113. A. Kumar, S.Gupta, V.D. Barhate. Extraction and spectrophotometric determination of Palladium (II) with isonitroso p-methyl acetophenone phenyl hydrazone (HIMAPH), *Oriental Journal of Chemistry*, **2010**, 26(3), 1085-1089.

114. D.B. Mandhare, V.D. Barhate. Extractive spectrophotometric determination of rhodium (III) with isonitroso p-methyl acetophenonephenyl hydrazine, *Oriental Journal of Chemistry*, **2009**, 25(4), 1125-1128.

115. D.B. Mandhare, V.D. Barhate. Extractive spectrophotometric determination of ruthenium (III) with isonitroso p-methyl acetophenone phenyl hydrazine, *Acta Ciencia Indica*, **2009**, 35(3), 325-329.

116. S.B. Zanje, A.N. Kokare, V.J. Suryavanshi, D.P. Waghmode, S.S. Joshi, M.A. Anuse. Development of a reliable analytical method for the precise extractive spectrophotometric determination of osmium (VIII) with 2-nitrobenzaldehydethiocarbohydrazone: Analysis of alloys and real sample. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **2016**, 169, 223-229. https://doi.org/10.1016/j.saa.2016.06.051

117. S.B. Zanje,V.J. Suryavanshi, A.N. Kokare, A.A. Ghare, G.S. Kamble, P.N. Kamble, M.A. Anuse. 2-Nitrobenzaldehyde Thiocarbohydrazone Assisted Precise Extraction Spectrophotometric Method for the Determination of Ruthenium (III) in Alloy and Catalysts. *Journal of Analytical Chemistry,* **2018**, 73, 438–451. https://doi.org/10.1134/S1061934818050131

118. S.B. Zanje, A.N. Kokare, V.J. Suryavanshi. Extractive Spectrophotometric Determination of Platinum in Cisplatin Injection, alloys and Catalysts Assisted by 2-nitrobenzaldehydethiocarbohydrazone, *Journal of Trace*

Analysis in Food and Drugs, **2016**, 1-24. http://dx.doi.org/10.7726/jtafd.2016.1001

119. S. S. Sawant. Sequential Separation and Spectrophotometric Determination of Osmium and Platinum with 5-Chloro-2-hydroxythiobenzhydrazide. *Analytical Sciences*, **2009**, 25(6), 813–818. https://doi.org/doi:10.2116/analsci.25.813
120. S.S. Shakuntala. Extractive Separation and Spectrophotometric Determination of Traces of Ruthenium from Mixtures Containing Excess Platinum Group Metals, *Analytical Letters*, **2009**, 42, 1678–1692. https://doi.org/10.1080/00032710902993803
121. R. Makhijani. Development of Extractive Spectrophotometric determination of Rhodium (III) using Schiffs Base as An analytical Reagent, *International Journal of Advanced Research in Science, Communication and Technology*, **2021**,6(2), 1101-1105. https://doi.org/10.48175/IJARSCT-1535
122. R. Makhijani. Development of Extractive Spectrophotometric determination of Iridium (III) using Schiffs Base as An Analytical Reagent, *Journal of Emerging Technologies and Innovative Research*, **2021**, 8(6),d643-d647.
123. R.M.Makhijai, V.D. Barhate. Extractive Spectrophotometric Determination of Ruthenium (III) with [N-(o-methoxy benzaldehyde)-2-Amino Phenol], *International Journal of ChemTech Research*, **2013**, 5(4), 1578-1584.
124. P. Khande, M. Thakur, M.K. Deb. Extraction of chloroplatinate(II) -2-[5-bromo-2-pyridylazo)]-5-diethylaminophenol-(TX-100)-N-hydroxy-N,N′-diphenylbenzamidine complex, *Journal of Scientific and Industrial Research*, **2005**, 64, 138-143.
125. A.Z. Abu Zuhri, B.F. Shraydeh, J. Shalabi. Selective Spectrophotometric determination of Palladium (II) with 2-(5-Bromo-2-Pyridylazo)-5-(diethylamino)-phenol. *Analytical Letters*, **2006**, 19 (1-2), 99-112. https://doi.org/10.1080/00032718608066244.
126. P. Ratre, D. Kumar. Spectrophotometric Determination of Complexation of Ruthenium (IV) with 2-[(5-Bromo-2-Pyridylazo)]-5-diethylaminophenol and N-hydroxy-N,N′-Diphenylbenzamidine, *International Journal of ChemTech Research*, **2014**, 6(1), 236-247.
127. R. Agnihotri, S. Akhtar, A. Singh, N. Agnihotri. *4H*-1-Benzoprans as Analytical Reagents- A Review, *Journal of Chemistry*, **2016**, 5(4), 22-31.
128. E. Pierpaoli, V. Viola, F. Pilolli, M. Piroddi, F. Galli, M. Provinciali. γ-and δ-tocotrienols exert a more potent anticancer effect than α-tocopheryl succinate on breast cancer cell lines irrespective of HER-2/neu expression. *Life Sciences*, **2010**, 86(17-18), 668-675. https://doi.org/10.1016/j.lfs.2010.02.018
129. E. Jr. Middleton, C. Kandaswami, T.C. Theoharides. The effects of plant flavonoids on mammalian cells: Implications for inflammation, heart disease, and cancer. *Pharmacological Reviews*, **2000**, 52(4), 673-751.
130. H. Lee, K. Lee, J.-K. Jung, J. Cho, E.A. Theodorakis. Synthesis and evaluation of 6-hydroxy-7-methoxy-4-chromanone- and chroman-2-carboxamides as antioxidants, *Bioorganic and Medicinal Chemistry Letters,* **2005**, 15(11), 2745-8. https://doi.org/10.1016/j.bmcl.2005.03.118
131. L. Costantino, G. Rastelli, M.C. Gamberini, J.A. Vinson, P. Bose, A. Iannone, M. Staffieri, L. Antolini, A. D. Corso, U. Mura, A. Albasini. 1-benzopyran-4-one antioxidants as aldose reductase inhibitors. *Journal of Medicinal Chemistry*, **1999**, 42(11),1881-93. https://doi.org/10.1021/jm980441h
132. G. A. Kraus, J. Mengwasser, W. Maury, C. Oh. Synthesis of chroman aldehydes that inhibit HIV, *Bioorganic and Medicinal Chemistry Letters*, **2011**, 21(5), 1399-401. https://doi.org/10.1016/j.bmcl.2011.01.031
133. A.K. Tiwari, M.V. Singh. New Insights into the origin and Therapeutic implications of Benzopyran and their derivatives: A review, *Biological and Medicinal Chemistry*, **2023**. https://doi.org/10.26434/chemrxiv-2023-q2641
134. M. Mohmad, N. Agnihotri, V.Kumar,M. Azam, R. Kamal, A. Kumar, U. Sharma, S. Javed, S. Murthu, K. Min. Preparation of a Pt(II)-3-Hydroxy-2-tolyl-*4H*-chromen-4-one Complex Having Antimicrobial , Anticancerous, and Radical Scavenging Activities with Related Computational Studies, *ACS Omega*, **2023**, 8(35), 31648-31660. https://doi.org/10.1021/acsomega.3c01316
135. K. Devi, N. Agnihotri, G. Kumar. Chemistry of Iridium (III)-3-hydroxy-2-tolyl-4*H*-chromen-4-one: The spectrophotometric analysis, radical scavenging activity and computational studies, *Indian Journal of natural Science,* **2024, 15,** 73193-73205
136. M. Mohmad, N. Agnihotri, V. Kumar, U. Sharma. A novel analytical, bioanalytical and theoretical approach to the platinum(II)-3-hydroxy-2-(4-methoxyphenyl)-4*H*-chromen-4-one complex, *Results in Chemistry*, **2023**, 5, 100767. https://doi.org/10.1016/j.rechem.2023.100767
137. M. Mohmad, N. Agnihotri. Bioanalytical and Theoretical Studies of the spectrophotometrically Investigated Iridium(III)-3-Hydroxy-2-(4-Methoxyphenyl)-*4H*-Chromen-4-one Complex, *Iranian Journal of Chemistry and Chemical Engineering*, **2023**, 42(10), 3383-3398.
138. N. Agnihotri, Mohini, S.I.Al Resayes, S.Javed, M.Azam,S.Kumar,S. Muthu,V.Kumar,M.Singh . A Spectrophotometric Determination and the Quantum Chemical Investigation of Pd(II)-3-hydroxy-2-(4-methoxyphenyl)-4-oxo-*4H*-1-benzopyran complex, *Bulletin of the Chemical Society of Ethiopia*, **2024**, 38(3), 591-603. https://doi.org/10.4314/bcse.v38i3.4
139. N. Kaur, N. Agnihotri, R. Agnihotri.3-Hydroxy-2-[2′-(5′-methylthienyl)]-4-oxo-*4H* -1-benzopyran for spectrophotometric determination of Tungsten(VI) and Palladium(II), *Vietnam Journal of Chemistry*, **2019**, 57(6), 686-695. https://doi.org/10.1002/vjch.201900069
140. M. Mohmad, N. Agnihotri, V. Kumar, R. Kumar. Iridium(III)-3-hydroxy-2-(3′-methyl-2′- thienyl)-4-oxo-*4H*-1-benzopyran complex: The analytical, *in-vitro* antibacterial and DFT studies, *Inorganic Chemistry Communications*, **2022**, 139(4), 109333. http://dx.doi.org/10.1016/j.inoche.2022.109333
141. M. Mohmad, N. Agnihotri, V. Kumar, M. Azam, S. M. Wabaidur, R. Kamal, R. Kumar, M. Alam, S. Kaviani. Radical scavenging capacity, antibacterial activity and quantum chemical aspects of the spectrophotometrically investigated iridium (III) complex with benzopyran derivative, *Frontiers in Pharmacology,* **2022**, 13, 945323
142. N. Kaur, N. Agnihotri, U. Berar. Microdetermination of Palladium(II) using 6-Chloro-3-hydroxy- 7-methyl-2-(2′-thienyl)-4-oxo-*4H*-1-benzopyran, *Asian Journal of Chemistry*, **2020**, 32(7), 1597-1602. https://doi.org/10.14233/ajchem.2020.22610
143. N. Kaur, R. Agnihotri, N. Agnihotri. Studies on the liquid phase extraction and spectrophotometric determination of 6-chloro-3-hydroxy-7-methyl-2-(2'-furyl) -4H-chromen-4-one complex of palladium(II), *Rasayan Journal of Chemistry*, **2022**, 15(1), 262-268. http://dx.doi.org/10.31788/RJC.2022.1516371
144. H. A. Shindy. Basics in colors, dyes and pigments chemistry: A review, *Chemistry International*, **2016**, 2(1), 29-36. http://dx.doi.org/10.31221/osf.io/y439u.
145. O.Tymoshuk, L. Oleksiv, O. Fedyshyn, P. Rydchuk, V. Matiychuk, T. Chaban. A New Reagent for Spectrophotometric Determination of Ir (IV): 5-[2-(4-hydroxyphenyl)hydrazineylidene]-4- iminothiazolidine-2-one (HPIT), *Acta Chimica Slovenica*, **2020**, 67(3), 970-976. http://dx.doi.org/10.17344/acsi.2020.6046
146. Yi, Yang. Catalytic kinetic spectrophotometric determination of trace iridiumIV in potassium periodate-xylenecyanol FF system, *Chemistry*, **2008**.
147. D. Revanasiddappa, K.T. Kumar. A highly sensitive spectrophotometric determination of platinum(IV) using leuco xylene cyanol FF, *Analytical and Bioanalytical Chemistry*, **2003**, 375, 319–323. https://doi.org/10.1007/s00216-002-1665-4
148. M. Rydchuk, T.Vrublevska, O.Korkuna, M.Volchak. Application of orange G as a complexing reagent in spectrophotometric determination of osmium (IV), *Chemia Analityczna*, **2009** , 54(5), 1051-1063.
149. S.H. Gaikwad, D.S. Bhange, M. Anuse. Extractive spectrophotometric determination of micro amounts of ruthenium(III) using 1,3-bis(hydroxymethyl)benzimidazole-2-thione:Analysis of fissium alloy, *Revue Roumaine de Chimie*, **2004**, 49(7), 631–639.
150. S.H. Gaikwad, U.B. Barache,T.N. Lokhande, M.A. Anuse. Experimentally validated extractive spectrophotometric determination method of osmium(VIII) from environmental samples: sequential separation of osmium(VIII), rhodium(III) and ruthenium(III), *International Journal of Environmental Analytical Chemistry*, **2020**, 102(17), 5179-5199. https://doi.org/10.1080/03067319.2020.1792893
151. S.H. Gaikwad, M.A. Anuse. A sensitive extractive spectrophotometric method for the determination of palladium (II) with 1, 3-bis (hydroxymethyl) bezimidazole-2-thione in catalysts, *Indian Journal of Chemical Technology*, **2003**, 10(5), 447-453.
152. A.B. Shaik, U.B. Barache, B.T. Khogare, R. Goswami, B.N. Kokare, P.P. Wadgaonkar, S.H. Gaikwad. Highly reproducible, simple and selective analytical method for extractive UV-visible spectrophotometric determination of ruthenium(III): Analysis of catalyst, fissium alloy and

sequential separation, *Spectrochimica Acta A,* **2020**, 243, 118814. http://doi.org/10.1016/j.saa.2020.118814

153. A. B. Shaikh, U. B. Barache, T. N. Lokhande, G. S. Kamble , M. A. Anuse, S. H. Gaikwad. Expeditious Extraction and Spectrophotometric Determination of Palladium (II) from catalysts and alloy samples using new chromogenic reagent, *Rasayan Journal of Chemistry*, **2017**, 10(3), 967-980. http://dx.doi.org/10.7324/RJC.2017.1031804

154. A.S. Amin, I.A. Zaafarany. Spectrophotometric determination of iridium after complexation and membrane filtration, *Analytical Chemistry Research*, **2015**, 3, 77-81. https://doi.org/10.1016/j.ancr.2014.10.001