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Review

Determination of rhodium: Since the origins until today Spectrophotometric methods

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Abstract

Anthropogenic emission of platinum group elements (PGEs) from the abrasion of automotive catalytic converters into the environment has significantly increased. Dust emitted from the catalyst is causing pollution problems of these metals in the future. However, the concentration level of these PGEs is still very low in the nature. The choice of which determination method to use depends on the levels of rhodium, the nature of the sample matrix and the availability of the instrument. In recent years, the development of analytical methods for the determination of rhodium has increased. This review reports the developments in UV–vis absorption spectrometry applied to the determination of rhodium.

Keywords: Rhodium determination; UV–vis absorption spectrometry; Catalytic and kinetic spectrophotometric; Review

Contents

1. Introduction

Efforts were carry out to assess their impact on the environment with respect to the emission of noble metals. During the first years of automobile catalyst impact research, the focus lay on platinum as the main component of Pt/Rh catalyst. Consequently, much effort invested in the development of analytical methods possessing sufficient detection capacity. Pt levels of a variety of environmental matrices already know, however, corresponding Rh data are mostly missing.

Rhodium is present at about $0.001\,\mu g\,ml^{-1}$ in the earths crust. Rh metal is known for its stability in corrosive environments, physical beauty and unique physical and chemical properties. Rhodium is now widely used in combination with platinum, in addition to or instead of palladium for automobile-exhaust emission con-

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trol catalyst. The platinum–rhodium ratio used about 11:1.

All platinum group element (PGE) species in solutions are highly co-ordinated and complex. The inertness of many complexes means that any ligand substitution requires strong conditions such as heating, high reagent concentration and long reaction times. The complexity of the chemical properties of the PGE and the kinetics of their reactions in solutions pose serious problems, especially for separations and preconcentration by liquid chromatography and their determination by spectrophotometric methods. A standard solution containing the PGE in definite oxidation states and chemical form is required for calibration of the analytical method used.

The use of spectrophotometric methods in rhodium analysis is limited due to low sensitivity. However, many new highly specific and selective organic reagents are being synthesised and various highly sensitive methods developed, increasing the applicability of these procedures.

This review summarises and discusses the analytical methods described in the literature, based on spectrophotometric techniques, for the determination of rhodium. The analytical methods for the determination of Rh fall into four main categories: (1) spectrophotometric methods; (2) kinetic catalytic spectrophotometric methods; (3) extraction spectrophotometric methods and (4) simultaneous determination of rhodium and other elements: (4.1) derivative spectrophotometric methods and (4.2) other methods of simultaneous determination.

2. Spectrophotometric methods

The application of UV–vis absorption spectrometry to the determination of precious metals is still popular in many laboratories, especially in developing countries. The technique provides easy determination of many metals from low to high concentrations at affordable cost. Many new organic reagents have been synthesized and various highly sensitive methods developed with molar absorptivities of 10^5–10^6 or even higher. In studies for establishing new methods, much attention paid to sensitivity. However, specificity and selectivity are also very important. Developing more methods with good selectivity will be beneficial for applications. Since in 1950s, numerous analytical methods proposed for the determination of rhodium. Analytical data for the methods not described in the text find in Table 1.

Most spectrophotometric determinations are based on the formation of coloured compounds or complexes by their reaction with unidentade or chelating ligands. These methods are usually not sufficiently sensitive, excepting for those involving charge transfer transition, as the sensitivity, in general, controlled by the extent of π-conjugation present in the ligand. Selectivity, most often, is achieved either by the proper choice of a reagent or by the use of masking agents. The sensitivity and selectivity can improve through the synthesis of organic ligands possessing extensively delocalized π-electron system along with appropriately placed ligating sites.

The mixed ligand systems make use of coloured complexes, charged or neutral, consisting of metal ion and two different ligands, one of these ligands is anionic and the other can be anionic or neutral [68].

The surfactant-sensitized systems are based on the ability of certain surfactants to sensitize the binary complexes of the metal ion with chromogenic ligands. The ligands, most often, are metallochromic indicators and for sensitization, cationic surfactants are used [69].

Basic non-chelating dyes enjoy high popularity in spectrophotometric analysis due to a high molecular extinction coefficient ($\approx 1 \times 10^5\,\mathrm{l\,mol^{-1}\,cm^{-1}}$). They are able to form extractable ion-pairs with monovalent or bivalent anionic complexes of metals leading to a variety of sensitive methods. Polivalent anionic metal complexes also react with basic dyes but polar solvents cannot extract the reaction products. Instead, the compounds formed accumulate during shaking on the phase boundary or on the wall of the separating funnel. The precipitate separate off and dissolved in a polar solvent, producing an intensily coloured solution that forms the basis of a flotation-spectrophotometric method of determination [70]. Marczenko and Kowalczyk describe two methods with malachite green [71]. The anionic Rh complex with $SnCl_2$ yields an ion associated with malachite green, on shaking the solution (in 6.5 M HCl) with benzene, the sparingly solution ion associated (Rh:malachite green = 1:2) precipitate at the phase boundary. The precipitate dissolved in a mixture of Me_2CO and H_2O (3 + 1). The molar absorptivity is $1.44 \times 10^5\,\mathrm{l\,mol^{-1}\,cm^{-1}}$ at 627 nm. When test solutions (0.65 M HCl) are shaken with diisopropyl ether, an ion associated of a different composition is formed (Rh:malachite green = 1:5) and the molar absorptivity is $3.4 \times 10^5\,\mathrm{l\,mol^{-1}\,cm^{-1}}$. Pt, Pd and Ir interfere except in small amounts.

Ion-association systems, in a more general way, could be said to result from the interaction of charged binary complexes with oppositely charged ions. When a neutral ligand, e.g. a nitrogenous base, is used, the primary complex produced is cation, possessing the same charge as that of metal. Such complexes were made to associate with anionic dyes like eosin, rose Bengal, etc. to form ion-associates that are extractable into organic solvents. When charged ligands, e.g. halides, thiocyanate or carboxylic acids, are used, the primary complex produced is anionic which can be associated with onium compounds like tetraphenylarsonium and phosphonium chlorides or cationic dyes. When the primary complex formed is anionic and coloured, they can be made to ion-associate with oppositely charged dye molecules. The particular advantage of such colour systems containing dye molecules over the onium salts is the increased sensitivity arising from the high molar absorptivity of the dyes, which usually lie in the range 6.0×10^4 to $1.25 \times 10^5\,\mathrm{l\,mol^{-1}\,cm^{-1}}$. The selectivity is also improved due to the inability of most

Table 1
Spectrophotometric method: analytical data

Reagents	Remarks		Sample	Reference
	λ (nm) pH	Range or DL (μg ml^{-1}) Absorptivity (l mol^{-1} cm^{-1})		
2-Mercapto-4,5-dimethylthiazole	– In HCl	– –	–	[1]
Sodium hypochlorite	665 4.7–7.2	5–20 –	–	[2]
Tin-(II) bromide	427 In HBr	0.4–4 –	–	[3]
Tin-(II) chloride	520 In HCl	– –	U-Rh alloys	[4]
Thiomalic acid	340 –	0.055 –	Synthetic samples	[5]
$NaBiO_3$	550–570 In acidic medium	20–60 –	Pt + 10% Rh alloy	[6]
N,*N*'bis(3-dimethylaminopropyl) dithio.ovrddot.oxamide	420 In HCl	– –	–	[7]
Symdiphenylcarbazone	565 3.0	0.1–2.1 6.17×10^4	–	[8]
5-Amino-2-benzimidazolethiol	390 2–5	0.5–4.0 –	–	[9]
Stannous iodide	460 In HCl	0.4–3 –	–	[10]
Hypobromite	530 11.2–11.3	10–60 –	-	[11]
Azide	405/480 5–8	2–40 –	–	[12]
Diphenylselenium oxide	512 –	– –	–	[13]
1-(2-Pyridylazo)-2-naphtol	– –	25–150[a] –	In presence of Pt, Au, Ag	[14]
Xylenol orange	528 2.7–3.3	– –	–	[15]
Hydrochloric acid	255 In HCl	5×10^{-6}–10^{-2}[b] 2×10^4	–	[16]
Nitroso R	490 5.5	2.06–10.4 1.312×10^4	–	[17]
Allthiox (8-alkylthioquinoline)	400 In H_2SO_4	0.08–1 7×10^3	–	[18]
1,2,4-Triazoline-3-thione	302 In HCl	1.5–13[a] $(3.2 \pm 0.1) \times 10^4$	–	[19]
4-Amino-5,7-disulfo-2,1,3-benzothiadiazole	550 –	– –	In presence of Ir	[20]
5-Sulfoallthiox (allyl ester of 5-sulfo-8-mercaptoquinoline)	430 In HNO_3	0.04–0.8 7.4×10^3	Pt-base alloys	[21]
8-Allylthioquinoline	400 –	– –	Niobates and titanates	[22]
EDTA	360 4–5	0–150 6.02×10^2	–	[23]

Table 1 (*Continued*)

Reagents	Remarks		Sample	Reference
	λ (nm)	Range or DL (μg ml^{-1})		
	pH	Absorptivity (l mol^{-1} cm^{-1})		
Cyclohexanediaminetetraacetic acid (CDTA)	356	0–150	–	[23]
	4–5	8.30×10^2		
Unithiol	315	20–200[a]	–	[24]
	–	–		
1-Nitroso-2-naphtol-3,6-disulfonic acid (nitroso-R salt)	450	–	–	[25]
	4.0	0.043[d]		
1,2-Dihydroxyanthraquinone-3-sulfonate (Alizarine Red S)	510	–	–	[25]
	4.0	0.011[d]		
Chromazurol S, $NaNO_3$, cetylpyridinium bromide	650	–	Pt-base Rh alloys	[26]
	HAc/Ac^-	–		
Di-2-pyridylglyoxal-2-quinolylhydrazone	–	0.0-9.2	In the presence of Pt-group metals	[27]
	3.0–5.5	–		
	–	–		
Bis(2-pyridyl)methanone 2-pyrimidylhydrazone	470	0–10.30	-	[28]
	1.5–3.5	1.64×10^4		
2-Thiobarbituric acid	327	–	–	[29]
	–	1.04×10^4		
Thiocyanate and Rhodamine 6G in gelatine	565	–	10% Rh–Pt and Pt thermocouple wires	[30]
	–	1.3×10^5		
Pyrocatechol	350/440	2–28	Sulphate electrolytes and wash waters of galvanic shops	[31]
	3–6	–		
Butaperazine dimaleinate, $CuSO_4$, ascorbic acid	465	0.2–28	–	[32]
	NaAc–HCl	2.44×10^3, 0.042[d]		
3-Hydroxi-3-[*p*-(dimethylamino) phenyl]-1-phenyltriazene	490	5.0×10^{-6}–5.0×10^{-5}[b]	–	[33]
	7.5	2.0×10^4, 0.0051[d]		
Propionyl promazine phosphate, Cu(II), ascorbic acid	470	0.1–18	Thermocouple wires and synthetic mixtures containing Pd, Ru, Os, U or Ir	[34]
	1.0–3.0	5.68×10^3, 1.8×10^{-3}[d]		
Propericiazine, Cu(II), ascorbic acid	460	0.1–32	Synthetic mixtures, such as the U–Rh alloy used in breeding reactors and the Rh–Ir fraction separated from Pt-group metal	[35]
	1.5–3.5	3.67×10^3, 0.028[d]		
$NH_2OH \cdot HCl$	512	–	High-rhodium platinum alloys	[36]
	In HCl	–		
Salicylfluorone and cetyltrimethylammonium bromide	595	0–0.4	Rh-active carbon and Rh-zirconia catalyst	[37]
	5.5–6.8	1.1×10^5		
2-(5-Bromo-2-pyridylazo)-5-(diethylamino)phenol	Dual-wavelength 597 and the reference 545	0–1	Electrolytic solutions of Rh–Pt alloys	[38]
	–	–		

Table 1 (*Continued*)

Reagents	Remarks		Sample	Reference
	λ (nm) pH	Range or DL (μg ml^{-1}) Absorptivity (l mol^{-1} cm^{-1})		
Stannous chloride and Rhodamine B	570–575	0.04–0.4	Rh-activated carbon catalysts	[39]
	In HCl	1.46×10^5		
2-(5-Bromo-2-pyridylazo)-5-(N-propyl-N-sulfopropylamino)phenol	557 and 600	–	–	[40]
	4.0–9.2	1.09×10^5 at 600 nm		
4,4′-Bis(diethylamino)thiobenzophenone, Triton X-100, ascorbic acid	512	0–1.4	–	[41]
	–	8.8×10^4		
Pyrazolone-(4-azo-2)-1-naphthol-4-sulfonic acid	–	–	In chloride and perchlorate solutions, and C fibers and electroplating wash waters	[42]
	–	–		
2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol	590	0–1.4	–	[43]
	5.0–7.0	9.0×10^4		
$SnCl_2$-malachite green	621	4–100[c]	Ore samples	[44]
	–	2.5×10^4		
α,β,γ,δ-Tetrakis(2-chlorophenyl)porphine	417	0–0.03	In Pt–Rh alloy after extraction separation with tributyl phosphate-CCl_4	[45]
	3	5.3×10^6		
Salicylaldehyde thiosemicarbazone	–	0.45–4.2	In different alloys and catalysts	[46]
	In KOH	–		
α,β,γ,δ-Tetrakis(4-sulfophenyl)porphine, Cd(I)	417	0–0.25	Catalysts	[47]
	8.0–10.0	5.9×10^5		
α,β,γ,δ-Tetrakis(4-trimethylammoniumphenyl)porphine	417	0–0.24	Catalysts	[48]
	9.0	5.17×10^5		
Rhodamine 6G in the presence of $SnCl_2$ and gelatine	558	0–0.48	–	[49]
	–	1.52×10^5		
2-[2-(5-Bromothiazolyl)azo]-5-dimethylaminobenzoic acid	674	0–0.48	Catalysts	[50]
	–	–		
2-(5-Bromo-2-pyridylazo)-5-dimethylaminoaniline	610	0–0.56	Catalysts	[51]
	2.8–6.1	1.5×10^5		
Meso-tetrakis(4-acetoxyphenyl)porphyrin, Cd(II), sodium dodecyl sulphate and Triton X-100	420	0–0.12	Catalysts	[52]
	9.5–10.5	8.78×10^5		
2-[2-(3,5-Dibromopyridyl)azo]-5-dimethylaminobenzoic acid	–	0–0.4	Catalysts	[53]
	5.0–7.0	1.29×10^5		
2-(2-Benzothiazolylazo)-5-diethylaminobenzoic acid	682	0–0.64	Catalysts	[54]
	4.3–5.5	1.0×10^5		
2-(2-Thiazolylazo)-5-diethylaminobenzoic acid	674	0–0.08	Catalysts	[55]
	4.0–6.5	1.44×10^5		

Table 1 (*Continued*)

Reagents	Remarks		Sample	Reference
	λ (nm) pH	Range or DL ($\mu g\,ml^{-1}$) Absorptivity ($l\,mol^{-1}\,cm^{-1}$)		
2-(3,5-Dichloro-2-pyridylazo)-5-dimethylaminoaniline	614 4.0–5.2	0–0.72 1.40×10^5	Catalysts	[56]
4-(2-Thiazoylazo)-2,4-diaminotoluene	590 3.7–4.9	0–0.5 1.1×10^5	Synthetic solution	[57]
5-(5-Nitro-2-pyridylazo)-2,4-diaminotoluene	583 4.1–6.5	0–0.64 1.7×10^5	Two types of catalysts	[58]
2,6,7-Trihydroxy-9-(3,5-dibromo-4-hydroxy) phenylfluorone and cetyltrimethylammonium bromide	610 5.8–6.7	0–0.5 1.29×10^5	Secondary alloy	[59]
Molybdate and nile blue	595 –	0–0.4 1.8×10^5	In some precious metal samples	[60]
2-(2-Thiazolyazo)-*p*-cresol in the presence of cationic surfactant	680 5.0	0.12–8 1.25×10^4	Catalysts	[61]
2-(3,4-Dichloro-2-pyridylazo)-5-dimethylaminophenol	596 5.0–6.4	0–0.8 8.7×10^4	Catalysts	[62]
2-(4-Antipyrinylazo)-5-diethylaminobenzoic acid	540 In HAc	0–2 3.20×10^4	Catalyst	[63]
Tungstate and rhodamine B in the presence of polyvinyl alcohol (PVA)	570 –	0–2 $>10^7$	Real samples	[64]
5-Bromo-(2-thiazolylazo)-5-diethylaminobenzoic acid in the presence of β-CD and cation surfactant CPB	687 4.75	0–0.6 1.14×10^5	Catalysts	[65]
1,2,3-Cyclohexanetrionedioxime	470 5	0.2–12.4 –	–	[66]
Phenanthrenequinone monosemicarbazone	– –	– –	–	[67]

DL, detection limit.

[a] μg.

[b] M.

[c] $ng\,ml^{-1}$.

[d] Sandell sensitivity in $\mu g\,cm^{-2}$.

other ions to react with two ligands to form an ion-association complex of the same nature as the desired ion [30,49,72].

Various α-substituted dioximes as dimethylglyoxime, α-benzyldioxime and furyldioxime were previously used for preparative purposes as well as for the spectrophotometric determination of Rh(III) [73–76]. The composition of rhodium(III) complexes with α-substituted alicyclic oximes were determined by the continuous variation method [77]. In this work, the electronic spectra of these compounds recorded and discussed. Sonic derivatives proposed for the spectrophotometric determination of rhodium. However, the alicyclic α-substituted dioximes, such as 1,2,3-cyclohexanetrionedioxime were less used in the analytical chemistry of Rh(III) than the other platinic metals, Rh(III) reacts with 1,2,3-cyclohexanetrionedioxime at high temperature to form yellow complex compound. This chelate was proposed for spectrophotometric determination of Rh(III) [66].

Shanina et al. develop a method for Rh determination in complexes with organic ligands and in organometallic compounds [78]. The sample decomposed by heating with H_2SO_4 containing HNO_3 or 57% $HClO_4$. The mineralization products were converted into the form for analysis by double boiling with HCl. Rh was then determined spectrophotometrically as a complex with 5-sulfoallthiox ($\lambda_{max} = 430$ nm) or as a complex with $SnCl_2$ and KI ($\lambda_{max} = 460$ nm).

For the determination of rhodium in hydro-formulation products, two methods examined: (1) spectrophotometry with $SnCl_2$ and (2) atomic absorption spectrometry with C_2H_2 air flame. The relative error was $\leq 5\%$ for determining 0.02–8 wt.% Rh by method (1). However, the method is slow (analysis time = 4.5 h). The relative error was 2.5–8% for determining 50–200 $\mu g\,ml^{-1}$ of Rh by method (2), which was much faster (approximately = 20 min) [79].

In other method, bipyridyl and phenanthroline complexes of Rh(III) were converted quantitatively into a form suitable for spectrophotometric determination of Rh with $SnCl_2$. The compounds tested subjected to thermal decomposition in air and the products of the pyrolysis fused with $K_2S_2O_7$. The fuse then dissolved in aqueous HCl and Rh determined spectrophotometrically by $SnCl_2$ method at 470 nm [80].

Several traditional methods recommended for the determination of precious metals in some specific objects. A method for quantitative determination of small quantities of Rh(III)-ions has been developed by Topalov et al. [81]. It based on the 470 nm peak absorbance of the complex formed between $RhCl_3$ and $SnCl_2$. The method has been used for monitoring the Rh(III) concentration change in photochemically treated solutions. A simple and rapid method for determining Rh in sulphate electrolytes developed by Parkhomenko et al. [82] not requiring the transformation of Rh sulphates into chlorides and the separation of extraneous ions. The determination of Rh in electrolytes is of interest in connection with the well-known determination of Rh as a blue–violet solution formed by the oxidation of Rh sulphate with sodium bismuthate in an acid medium. Rh can be determined without prior dissolution of the electrolytes which decreases the error in the determinations. Neither masking nor separation of interfering elements is required. The correctness of the results of Rh determination in electrolytes and Rh electroplating baths by the developed method were monitored by the atomic absorption method.

In other study, solvent effects on the complexation (rate and resultant colour intensity) of rhodium(III) with heterocyclic azo compounds in aqueous–organic media were examined [83]. The colour reaction enhancement by alcohols used for developing spectrophotometric methods for determining Rh 0.03–1.2, 0.05–1.6 and 0.3–5.0 $\mu g\,ml^{-1}$ in chloride, perchlorate and sulphate solutions, respectively. The method used for determining Rh in waters of electroplating plants.

Lazarev and Gerko [84] developed a method for Rh determination in wash waters of rhodium plating baths. An ion pair is formed by addition of $SnCl_2$ and chrompyrazol I, which has a molar absorptivity of $10.5 \times 10^4\,l\,mol^{-1}\,cm^{-1}$ at 630 nm. The addition of non-ionogenic surfactants enhances the stability of the optical absorptivity.

The effect of the state of Rh(III) ions in solutions, of the nature of reagent and labelling agents on the formation rate and yield of the stained complexes used in photometric analysis was considered. The transformation of inert forms of Rh(III) into active aqua–acidic complexes increase the sensitivity and expressiveness of photometric methods of its detection and provide for the correctness and reproducibility of the analytical results [85].

During the two past decades flow injection analysis (FIA) has rapidly grown in popularity. This is because of its simplicity, versatility, precision, high sampling rate, low sample consumption, low cost and ease of automation. This technique involves the injection of the sample into a stream of chromogenic reagent and ligand, which transports it to the detector. The analysis requires a small amount of sample (10–300 μl), which together with a light of 10 mm usually used, is responsible for relatively high sensitivity. Virtually each colour reaction in a homogenous medium, provided it is sufficiently fast, can be adapted to flow injection-processing resulting in a flow injection spectrophotometric method. Flow injection applied to the determination of precious metals only relatively recently. There are few reports in this area, but some promising developments made by coupling an efficient preconcentration procedure with an adequate on-line detection method. A flow injection method has been developed based on its catalytic effect on the oxidation of nile blue by periodate at pH 9.20. The reaction monitored spectrophotometrically at 630 nm. The proposed method has been used for the determination of rhodium(III) in synthetic samples with satisfactory results [86].

A highly sensitive method by laser thermal lens spectrometry based on the colour reaction between Rh and the new chromogenic reagent 5-bromo-(2-thiazolyazo)-5-diethylaminobenzoic acid (5-Br-TADEB) was developed [87]. The experimental results show that in a acetic/acetate buffer solution of pH 4.0–5.7, and in the presence of acetone, Rh reacts with 5-Br-TADEB to form a 1:2 stable blue complex exhibiting an absorption maximum at 632 nm which is well-matched to the wavelength of the laser beam used ($\lambda = 632.8$ nm). The detection limit and linear range are 0.004 $\mu g\,ml^{-1}$ and 0.01–0.08 $\mu g\,ml^{-1}$, respectively. The method also applied to determine Rh in catalyst samples with satisfactory results.

New gravimetric, oxidimetric and spectrophotometric methods for the determination of Rh as $[Rh(Rod)_2Cl_2][Cr(NCS)_4(amine)_2]$ were developed by Ganescu et al. [88]. The association complex involved in these methods has a well-determined composition, a very good thermal stability and is soluble in organic solvents. These methods applied for the determination of Rh in ores, alloys and catalyst in the presence of the other Pt or transitional metal ions. In addition, the experimental results statistically evaluated.

Balcerzak presents a review, with 57 references, which describe the analysis of platinum-group metal using tin chloride [89]. Platinum metals, in hydrochloric acid medium, react with $SnCl_2$ by forming anionic complexes containing $SnCl_3{}^-$ or $SnCl_3{}^-$ and Cl^- ligands. The complex anions are more labile compared to simple chloride complexes. They are suited for methods of separation and spectrophotometric determination of platinum metals.

3. Kinetic catalytic spectrophotometric methods

Kinetic catalytic methods are proved to be an attractive analytical tool combining high sensitivity and simplicity of metal determinations. An important component of further development of kinetic methods is due to searching for advanced approaches for selection of suitable reactions to be used for the determination of a specific metal ion. Amongst the possible types of catalytic reactions, the widest use received redox reactions. Prediction of the behavior of redox catalytic systems can take place along two main directions. Whereas a more traditional approach deals with evaluating the redox potentials for reactants, an alternative way is based on the investigation of their chemical forms in reaction mixture. The reaction ability of a metal ion and, in particular, its catalytic activity is largely dependent on the forms in which the metal exists in solution. Therefore, distinguishing a species of the metal ion, which displays the catalytic effect, may provide a better insight into the mechanism of the catalityc reaction. Given that such a metal species is defined, both the choice of conditions for kinetic determination, selectivity control and enhancement of the sensitivity would become greatly facilitated.

Rh catalyses the oxidation of Cu(II)–Cu(III) by IO_4^- at pH 8.5–9.5. The extent of the reaction can be determined from the absorbance at 413 nm [90]. The determination of Rh based on this effect. Pt, Pd, Ir and Au do not interference.

Davydova et al. describe a highly sensitive pre-concentration method for the determination of ultramicro amounts of PGEs in rocks by using a combined procedure of fire assay into Ni_2S_3 followed by adsorption of the noble metals on the chelate sorbent PVB-MP-20T and coprecipitation with thiourea [91]. This pre-concentration procedure in combination with catalytic methods of determination allows the determination of PGEs and at the same time shortens the analysis time.

The iodine-azide reaction is induced by 2-mercaptopurine; Ir(IV) eliminates the induction effect by complex-formation through the S atom. Ir can thus be determinate at 0.01–0.4 $\mu g\,ml^{-1}$. In contrast, complex formation between Rh(III) and 2-mercaptopurine yields a product which induces the reaction in proportion to the Rh concentration. This effect permits Rh determination at 0.2–10 $\mu g\,ml^{-1}$ with ±3% error [92].

Zhitenko et al. propose a method based on its catalytic action on oxidation of methyl orange by sodium periodate in a weakly acidic solution in the presence of phosphate as activator [93]. The method used for determining Rh in standard references and technological samples.

Cai et al. recommend a new method for the determination of rhodium by flow injection analysis [94]. The proposed method is based on the catalytic action of Rh(III) on the oxidation of α-naphtholphthalein with KIO_4.

Other procedures summarized in Table 2.

Since the precious metals are excellent catalysts, many workers have long investigated catalytic kinetic methods of these metals. The indicator reactions in these methods were usually monitored by photometry. These methods are very sensitive, many of them giving detection limits of 0.01–0.1 $ng\,ml^{-1}$. However, they usually suffer severely from interferences from many other ions and often require strict control of the experimental conditions and complete remove of interferences. A review relating to the application of kinetic methods for the determination of platinum group metals for rapid monitoring of technological processes has been published [110].

Diverse kinetic determinations based in the catalytic action of rhodium described in the literature. First applications of the kinetic methods to the determination of rhodium appear in the bibliography in 1970 [111,112] and 1975 [113], in which the conditions for the kinetic determination of rhodium after separation of its sulphate complex by thin-layer chromatography are given. Some of the reactions that they have served as base for this type of determinations are collected below:

- Oxidation of methyl red with periodate [114,115]. In the first reference, the method accuracy checked by the analysis of model solutions and standard reference materials.
- Cu(II) was catalitically oxidised by periodate in copper- and nickel-based samples without rhodium separation in the presence of excess noble and accompanying metals and after copper–nickel matrix separation by precipitation of hydroxo carbonates [116]. The method was used for analysis of electrolytic and ore beneficiation samples.
- Accelerating effect of the Rh on the reaction of Ce(IV) with hydrogen peroxide, whereas platinum, on the basis of its inhibitory effect on the same reaction in the presence of rhodium [117]. Rh/Pt mixtures containing these elements in ratios from 1:1.9 to 1:7.5 were analysed in one kinetic run.
- Based on monitoring the decrease in the absorbance of rhodamine B at 555 nm associated with its oxidation by potassium periodate in the presence of Rh as a catalyst [118].
- Catalytic effect on the oxidation of butylrhodamine B by KIO_4 [119].
- Catalytic effect on the oxidation of ethylrhodamine B by KIO_4 on heating in NaCl and H_3PO_4 solution with the result of decolouration [120].
- In the presence of rhodium, arsenazo III can be oxidised by KIO_4 in HAc–NaAc medium [121]. The new catalytic kinetic method based on the decolourization reaction of arsenazo III.
- Rh(III) had catalytic action on the decolouration of nile blue oxidised with KIO_4 under heating in H_3PO_4 solution in the presence of NaCl [122].

Table 2
Catalytic spectrophotometric methods: analytical data

Reagents	Remarks		Sample	Reference
	λ (nm)	Range (μg ml^{-1})		
	pH	Detection limit (μg ml^{-1})		
Rhodamine B–hydrogen peroxide	–	0–0.6	Catalysts, rhodium electroplating solutions	[95]
	4.5–5.0	6.71×10^{-4}		
Decolouration reaction of thorin and KIO_4	490	$(0.12–4.5) \times 10^{-3}$	Synthetic and catalyst samples	[96]
	3.9	0.06×10^{-3}		
Sulfarsazene oxidation with KIO_4	–	10^{-5}–10^{-3}	In model solutions using the added-founded method	[97]
	3.6	–		
Oxidative decolouration of 2-(4-chloro-2-phosphonophenyl)azo-7-(2,4,6-trichlorophenyl)azo-1,8-dihydroxy-3,6-naphthalenedisulfonic acid by $KBrO_3$	550	$(1–50) \times 10^{-3}$	Platinum-rhodium catalyst	[98]
	Acid medium	1.08×10^{6}[a]		
Oxidation of methyl orange or sulfarsazene with $NaIO_4$ in a continuous-flow system	–	10^{-3}–10^{-2} and 0.5×10^{-3}-10^{-2}, respectively	State standard reference samples	[99]
	–	–		
Oxidative decolouration of arsenazo-DCB by $KBrO_3$	520	0.02–0.20	Pt–Rh catalyst	[100]
	H_2SO_4	–		
Oxidation of *N*-methyldiphenylamine-4-sulfonic acid by KIO_4 with photometric signal control	–	5.0×10^{-3}–4.8×10^{-2}	In complex materials: artificial mixtures of various components and an industrial sample of a platinum concentrate	[101,102]
	2.5–3.5	–		
Decolouration of chlorophosphonazo-PN oxidized with KIO_4	540	0.002–0.008	Pt–Rh catalyst	[103]
	Acid medium	0.001		
Oxidation of nile blue by periodate	630	$(10–850) \times 10^{-3}$	Synthetic and real samples	[104]
	9.0	8×10^{-3}		
Oxidation of basic dyes (ethylrhodamine B, butylrhodamine B, nile blue) with KIO_4 in NaCl	–	0.08–0.16, 0–0.18, 0–0.24	–	[105]
	H_3PO_4 solution	2.24×10^{-4}, 2.84×10^{-4}, 3.80×10^{-4}		
Oxidative fading of chlorophosphonazo-pA with $KBrO_3$	–	$(5–30) \times 10^{-3}$	Pt–Rh catalyst	[106]
	Acidic medium	5×10^{-3}		
Oxidative colour reaction of diantipyryl-(*p*-dimethylamino)-phenylmethane with KIO_4	–	$0\text{-}80 \times 10^{-3}$	Catalysts	[107]
	H_3PO_4 medium	6.20×10^{-4}		
Oxidative fading reaction between *p*-acetylcarboxylazo and KIO_4	550	$(5–100) \times 10^{-3}$	Pt–Rh catalyst	[108]
	Acid medium	6.2×10^{5}[a]		
Oxidation of triphenylamine-4-sulfonic acid by $NaIO_4$	–	–	Synthetic mixtures	[109]
	3	–		

[a] Molar absorptivity.

- Based on the catalytic effect of Rh on the oxidative colour reaction of diantipyryl (*p*-diethylamino) phenylmethane with KIO_4 in the H_3PO_4 medium and 90 °C water bath [123].
- Based on the catalytic effect of Rh on the oxidative colour reaction of diantipyryl-3,4-(dibromo)-phenylmethane with $KBrO_3$ in phosphoric acid medium in boiling water bath [124].
- Oxidation of *o*-toluidine blue by periodate in micellar media. The reaction monitored spectrophotometrically by measuring the decrease in absorbance of *o*-toluidine blue at 628 nm with a fixed-time method [125].
- Based on catalytic oxidation of malachite green with sodium periodate and monitoring at 617 nm during 3 min with the fixed time method [126].
- Catalytic action on the oxidative fading reaction between acridine red and potassium periodate in sodium tetraborate medium [127].
- Catalytic oxidation of methyl orange or sulfarsazene with $NaIO_4$ in the continuous-flow mode [128].

4. Extraction and spectrophotometric methods

Knowledge of oxidation states and ligands, as well as of the speciation of rhodium with other compounds, is essential in designing new recovery techniques. For example, the separation and purification of rhodium from other PGEs by solvent extraction is one of the most difficult areas in the refinement of precious metals.

Solvent extraction has been widely used for separation of the platinum metals in chemistry and industry for many years. These noble metals recovered from a wide variety of sources that present metallurgical problems of a widely differing nature. The aqueous chemistry of these metals is extremely complex. The most prominent feature of the chemistry is the very great tendency of the metals to form chloro-complexes in chloride media.

The complex nature of solution chemistry of PGEs has contributed to the difficulty of developing methods for their separation from binary or multicomponent systems. Of these metals, use the differences in their kinetic behaviour for the formation of extractable species, as well as the strength of electrostatic interaction of their chloro-complexes with liquid ion exchangers or with oxygen containing solvents. The study of the chloro-complexes of the PGEs clearly indicates that the strength of the interaction with ion exchangers is highly dependent on the charge of the complex and depends on the age of the solution of rhodium. Therefore, the rhodium(III) chloro-complex is also poorly extracted which is due to the charge of the complex as well as its labile character toward aquation. Hence, it is worthwhile to develop the solvent extraction procedure in weak organic carboxylic acid media. One of the distinct advantages of the organic acid media is the facility of controlling the concentration of complexing ligand, the ease of adjustment of pH and wide difference in pH at which various metal form anionic complexes. The comparative ease of stripping of the complexes from the organic phase can be achieved by fully exploiting the differences in reactivity of various metals to backwash in the aqueous phase by mineral acid. It known that organic acid media offer better separation of metals possibly due to high stability of metal organic acid complexes. In hydrochloric acid solutions with higher acidity, rhodium exists in the form of $RhCl_6{}^{3-}$. Carrying three negative charges, it closely surrounded by water molecules and very difficultly extracted by organic solvents. Hence, research reports on the extraction of rhodium are limited. Berg and Senn [129] pointed out that the percentage of Rh(III) extracted by tributylphosphate (TBP) is very low. Chen et al. [130] obtained the similar result. The extraction of Rh(III) with TBP after adding stannous chloride in hydrochloric acid solution is studied by Zou et al. [131], an efficient stripping method as well as a description of the extraction mechanism is given. When the amine extractants, of which the basicity is stronger than that of TBP, were used to extract Rh(III), Fedorenko and Ivanova [132] and Khattak and Magee [133] obtained, respectively, about 75–80% extraction from 0.1 M HCl solution by tri-*n*-octylamine (TOA).

Even if the quaternary ammonium salt that possesses the strongest basicity among the amines used as extractant, the maximum extraction yield of rhodium achieved by Work and Good [134] also does not exceed 80%. In recent years, Demopoulos [135], Benguerel et al. [136] and Ashrafizadeh and Demopoulos [137] have carried out a series of investigations on Rh extraction in HCl solution by Kelex 100 or TOA, and given a critical review on the complex aqueous chemistry of rhodium in chloride solution, with special emphasis on speciation [138]. The extraction result of rhodium can be greatly improved by adding a ligand with a large volume, such as $SnCl_3{}^-$, $SnBr_3{}^-$ and SCN^-. Demopoulos et al. [139], Benguerel et al. [140] and Ashrafizadeh and Demopoulos [141] have proposed a new method to extract Rh(III) using Kelex 100 after adding stannous chloride to the feed solution. However, the effects of stripping from the loaded organic phase with HNO_3 or $H_2SO_4 + Na_2SO_4$, or with $Na_2SO_3 + HCl$ are not satisfactory.

The value of rhodium as a precious metal has prompted several investigations into its separation and preconcentration. Rh is determined spectrophotometrically at 430–435 nm as the amber-to-red complex of Rh(II) with 4,5-dimethyl-2-mercaptothiazole in 3–9 M HCl after reduction from Rh(III) by $SnCl_2$ or $CrCl_2$. If $SnCl_2$ is the reductant, Rh is quantitative separated from Ir by $CHCl_3$ extraction [142]. Separations made in solutions that fumed with H_2SO_4 if $CrCl_2$ (but not $SnCl_2$) used for reduction of Rh. After removal of the $CHCl_3$, the complex dissolved in diluted HCl and the absorbance is determinate. Beer's law obeyed if the solutions are freshly prepared.

Diamantatos and Verbeek [143] describe a procedure for the separation of platinum, palladium, rhodium, iridium and gold by solvent extraction. The scheme applied to the separation of the metals from a synthetic solutions and spectrophotometric determination.

Rh(III) was determined in solutions containing Co, Cu, Ni and Fe by extraction and spectrophotometry [144]. The methods involved rapid precipitation of Co, Cu, Ni and Fe by 0.01 M α-furildioxime (I) or α-furilmonooxime (II) at pH 4 or 5, respectively. Removal of the precipitate by extraction with $CHCl_3$, heating the aqueous phase with excess I or II to 95–98 °C for 30 min, measuring the absorbance of the 1:2 Rh-I complex at 360 nm (molar absorptivity 2.0×10^4) or extracting the 1:2 Rh-II complex into $CHCl_3$ and measuring its absorbance at 385 nm (molar absorptivity 3.05×10^4).

The extraction and determination of noble metals by using high molecular weight amine (HMWA) extractants is well known but little work is reported on the extraction of rhodium(III), particularly by secondary amines. The use of *n*-octylaniline in the extraction of noble metals describe in diverse works [145,146]. The comparison can be made of the merits of *N*-*n*-octylaniline relative to *n*-octylaniline as an extractant. These are: (a) the method of preparation; (b) more equilibrium time; (c) higher reagent concentration; (d) requires multiple extraction for complete recovery of noble metals and (e) use of mineral acids which is not environmental friendly.

Kolekar and Anuse describe recent investigations that involve the formation of very stable complexes of rhodium(III) with weak organic acid like sodium salt of malonic acid prior to solvent extraction [147]. In the novel separation method identified, aquo-chloro complexes of rhodium(III) converted into more stable rhodium malonate complexes, which undergo aquation to a lesser extent, making them more easily extracted. The use of weak carboxylic acids opens up new options for the separation of rhodium from iridium and other PGEs. *N*-*n*-octylaniline is a secondary amine, which acts as liquid anion exchanger. *N*-*n*-octylaniline-malonate system was studied to investigate the extraction of aqueous rhodium(III) solution as a function of various parameters. The proposed method is used for rapid and selective separation of rhodium(III) from associated elements in their binary and ternary mixture. It is also tested for the separation and determination of rhodium(III) from real samples as alloy.

Gao et al. propose a method based on the formation of complex of Rh(III) with $SnCl_2$ and 2-mercaptobenzothiazole in aqueous solution and extraction of the complex with *n*-propanol–NaCl–H_2O system [148]. The extraction conditions studied and optimised. The absorption maximum of the complex was at 456 nm, the linear range 0–40 $\mu g\,ml^{-1}$, and the molar absorptivity $1.2 \times 10^4\,l\,mol^{-1}\,cm^{-1}$. The extraction rate of Rh(III) reached up to 99% in the medium of HCl, and the proposed method can separate Rh from matrix metals of Fe, Al, Pb, Zn and Ca, etc. The method was used in the determination of Rh(III) in ZrO_2 supported catalyst.

The effects of knowledge of the solution chemistry of the platinum metals on their separation by solvent extraction and ion exchange methods reviewed, for the period 1950–1983 [149]. The review concentrates on the chloro-complexes of these metals and indicates those areas, which need more investigation or interpretation to provide adequate separation methods.

Other determinations achieved describe in Table 3.

5. Simultaneous determination of rhodium and other elements

5.1. Derivative spectrophotometric methods

Derivative spectrophotometry used to increase the selectivity and sensitivity of the determination of various substances whose absorption spectra overlap. Interest in the analytical applications of derivative spectrometry has been on the increase for the past few decades, owing to the introduction of commercial spectrometers capable of operating in the derivative mode.

The increased selectivity in derivative spectrophotometry results from the fact that bands, which overlap in normal absorption spectra appear as separated bands in the derivative spectra. Derivative spectrophotometry can increase the sensitivity owing to the amplification of derivative signals and lowering of noise.

The different determinations achieved describe in Table 4.

5.2. Other methods of simultaneous determination

In the bibliography are collected numerous investigations in those which are attempted to carry out the mixtures resolution of rhodium with different metallic ions.

A method for simultaneous determination of trace Rh and Co by using 5-(5-nitro-2-pyridylazo)-2,4-diaminotoluene (5-NO_2-PADAT) as colour reagent was developed. The method was based on the reaction of Co(II) and Rh(III) with 5-NO_2-PADAT in HAc–NaAc buffer solution of pH 5.5 at room temperature and in a boiling water bath to form a complex. This method applied to the simultaneous determination of trace Co and Rh in synthetic samples [191].

With respect to the determination of Rh and Ir, there are several references between those, which fit to emphasise the following: dual-wavelength spectrometry for Rh and Ir recommended with extraction of their complexes with $SnBr_2$ and 2-mercaptobenzothiazole into ethyl acetate and used for the determination of these elements in metallurgical intermediate products [192]. The other is summary in Table 5.

The determination of Rh and Os carried out by mathematical or graphical processing of absorbance values at wavelengths properly selected by using nitroso-R salt [202].

Iterated target transformation factor analysis was applied to resolve the overlapping spectral data and led to the simultaneous determination of Rh and Pd after developing their colour with 2-(5-bromo-2-pyridylazo)-5-dimethylaminophenol and Triton X-100 [203]. The methods not described in the text found in Table 5.

Table 3
Extraction and spectrophotometric methods: analytical data

Reagents and organic solvents	Remarks		Samples	Reference
	λ (nm) pH	Range (μg ml^{-1}) Absorptivity (l mol^{-1} cm^{-1})		
1-Nitroso-2-naftol in $CHCl_3$	300 or 418 –	0–2 –	–	[150]
$SnBr_2$ by isoamylic alcohol	429 $HClO_4$/HBr	– –	–	[151]
2-Mercaptobenzimidazole in BuOH	360 –	– –	In presence of Ir	[152]
2-Thenoyltrifluoroacetone and extraction in xylene	430 –	– –	–	[153]
Diantipyrinylmethane and iodide and extraction in $C_2H_4Cl_2$	495 –	– –	–	[154]
1-(2-Pyridylazo)-2-naphthol in $HCONMe_2$ and extraction in $CHCl_3$	600 or 640 –	– –	In presence of platinum metals, gold and silver	[155]
Diethyldithiocarbamates in $CHCl_3$	427 –	≤2 0.0039[a]	Rocks	[156]
$SnCl_2$ in HCl and extraction into tri-*n*-octylamine in CCl_4	415 In HCl	0.4–3.0 –	–	[157]
Acenaphthenequinone monoxime in $CHCl_3$	390 4.4–6.0	– 0.0036[a]	–	[158]
Di-*o*-tolylthiourea in presence $SnCl_2$ and extraction by various organic solvents	400 In HCl	0.2–16 $(1.47 \pm 0.03) \times 10^4$	–	[159]
N-α-pyridyl-*N*′-benzoylthiourea in $CHCl_3$	360 5.24–6.3	0.69–6.9 9.54×10^3, 0.0102[a]	In the presence of most of base metals and all other Pt metals	[160]
α-Benzoinoxime in $CHCl_3$	390 2–8	5–35 –	–	[161]
p-(Dimethylamino)benzylidenerhodanine in nitrobenzene	535 In HCl	0.01–0.2 $(9.97 \pm 0.44) \times 10^4$	–	[162]
N-phenyl-*N*′-(α-pyridyl)thiourea in BuOH	335 1–6	0–14 2.86×10^4	In the presence of Ir, Pt and Pd	[163]
Ethyl-α-isonitrosoacetoacetate into MeCOEt	390 –	– –	–	[164]
4-*S*-benzyl-1-*p*-chlorophenyl-5-phenyl-2,4-isodithiobiuret in $CHCl_3$	375 In HCl	0.1–10.0 1.70×10^4	–	[165]
1-Phenyl-3-thiobenzoylthiocarbamide in different solvents	325 –	0–5 3.1×10^4	–	[166]
4,4′-Dihydroxybenzophenone thiosemicarbazone in benzyl alcohol	430 –	– –	–	[167]

Table 3 (*Continued*)

Reagents and organic solvents	Remarks		Samples	Reference
	λ (nm) pH	Range (μg ml^{-1}) Absorptivity (l mol^{-1} cm^{-1})		
Carbonylchlorobis (triphenylphosphine) in $CHCl_3$	420	–	–	[168]
	–	–		
Dithizone in $CHCl_3$	560	6×10^{-3}–60×10^{-3}[b]	–	[169]
	8.5	2.92×10^4		
N-α-(5-bromopyridyl)-*N*′-benzoylthiourea in 1:10 EtOH–$CHCl_3$	350	0.44–4.4	–	[170]
	Acetate medium	1.519×10^4, 0.005[a]		
$SnCl_2$ and 2-mercaptobenzothiazole in Et acetate	446	0–2.4	A synthetic sample containing 5 mg each of Pt, Pd, Au, Ag and 20 and 52 μg Rh	[171]
	In HCl	1.55×10^4		
HBr, tribenzylphosphine oxide, $SnCl_2$ in $CHCl_3$	400	1–20[c]	–	[172]
	In HBr	2.6×10^4		
$SnCl_2$, rhodamine 6G, in solvents of low polarity	530	0.04–0.5	–	[70]
	In HCl	4.0×10^5		
Diphenylcarbazide in presence of α-picoline into iso-BuCOMe	560	0.1–3	–	[68]
	–	4.01×10^4		
α-Benzilmonoxime in $CHCl_3$	400	–	Samples containing excess Cu, Ni, Co and Fe	[173]
	2.8	3.0×10^4		
4-(2-Pyridylazo)resorcinol in the presence of micellar hexadecylpyridinium bromide	520	0.08–1.00	–	[69]
	–	55×10^{-3}[a]		
3-Hydroxy-2-methyl-1,4-naphthoquinone monoxime into molten naphthalene	430	0–6.06	Synthetic solutions containing known amount of Rh and varying amounts of foreign ions	[174]
	5.5–7.0	2.15×10^4, 0.0046[a]		
2-Mercaptobenzimidazole in $CHCl_3$	385 or 400	0.3–4	In the presence of iridium	[175]
	–	–		
Isonitroso-*p*-methylacetophenone in $CHCl_3$	370	0.05–6	–	[176]
	4.2–6.5	2.47×10^4, 4.2×10^{-3}[a]		
Di(2-ethylhexyl)phosphoric acid	–	–	Separation from ruthenium and iridium	[177]
	4.05	–		
4-(Non-5-yl)pyridine	–	–	Extraction of rhodium and iridium	[178]
	In H_3PO_2	–		

[a] Sandell sensitivity in μg cm^{-2}.
[b] mol l^{-1}.
[c] μg.

The determination of rhodium in Pt–Rh alloy by dual-wavelength differential spectrophotometric method was studied [224]. The colour complex of Rh with stannous chloride formed in hydrochloric acid solution. The effects of HCl concentration, temperature, content of $SnCl_2$, standing time and diverse ions on the determination of rhodium also examined. The selected wavelengths were 410 and 470 nm. This method successfully used in determining rhodium in the range of 4–30% in Pt–Rh alloy.

The direct dual- and tri-wavelength spectrophotometric determination of microamounts of platinum and rhodium studied. EtOAc [225] extracted their complexes with $SnCl_2$

Table 4
Derivative spectrophotometric methods: analytical data

Elements and reagents	Remarks	Samples	Reference
Rh with ortho-hydroxyhydroquinonephthalein in presence of *N*-hexadecylpyridinium chloride	Third derivative, measuring the distance on the peak at 530 nm and the troughs at 50 nm and 560 nm, $7.37 \times 10^5\,\mathrm{l\,mol^{-1}\,cm^{-1}}$	–	[179]
Rh meso-tetrakis(*p*-sulfophenyl)porphyrin in presence of cetyltrimethylammonium bromide	Fourth derivative at 416.5 nm, in pH 9 borax buffer solution, $1.4 \times 10^7\,\mathrm{l\,mol^{-1}\,cm^{-1}}$, detection limit is $5\,\mathrm{ng\,ml^{-1}}$	Ores after its pre-concentration by fire assay and solvent extraction	[180]
Rh pre-concentration with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol chelate/tetraphenylborate ion pair on microcrytalline naphthalene	Third derivative, in the pH range 3.3–5.8, detection limit is $20\,\mathrm{ng\,ml^{-1}}$	Various synthetic samples	[181]
Rh adsorption of its 1-(2-pyridylazo)-2-naphthol complex on microcrystalline naphthalene	First derivative, in the pH range 4.2–5.5, detection limit is $30\,\mathrm{ng\,ml^{-1}}$	Various synthetic samples	[182]
Rh 2-(2-thiazolylazo)-5-dimethylaminobenzoic acid and Triton X-100	Third derivative, in the pH range 5.2–6.8, the slope of the calibration plot is 1.26	Various synthetic samples	[183]
Rh and Au *p*-dimethylaminobenzylidene rhodanine in presence of cetyltrimethylammonium bromide	Review	Various synthetic samples	[184]
Rh and Ir 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol onto microcrystalline naphthalene	Zero-crossing technique measurement, in the pH range 5.0–6.5 and 3.5–5.5, respectively, detection limits are 72 and 133 ng	Various synthetic samples	[185]
Rh and Pd 5-(3,4-methoxyhydroxybenzylidene)rhodanine in the absence and presence of cetylpyridinium bromide	Detection limits are 1.2 and $5.6\,\mathrm{ng\,ml^{-1}}$, respectively	Various synthetic samples	[186]
Rh and Pd 2-(5-bromo-2-pyridylazo)-5-(diethylamino)phenol	Rh by first derivative peak-peak values at 560–700 nm, in phosphoric acid medium after heating in boiling water for 120 min and cooling and Pd by absorbance at 631.2 nm at room temperature	Catalyst	[187]
Rh and Pd 5-(2,4-dihydroxybenzylidene)rhodanine	Normal and first derivative, In the pH range 5.0–5.5 and 10.4–10.8, 7.4×10^4 and $9.0 \times 10^4\,\mathrm{l\,mol^{-1}\,cm^{-1}}$ at 558 and 460 nm, respectively	Silicate rocks	[188]
Rh and Ru octadecyl dithiocarbamate	First derivative, zero-crossing measurement	Ores and minerals	[189]
Rh, Pd and Pt in binary mixtures with $SnCl_2$	Derivative methods in aqueous solutions or after extraction into 1,2-dichloroethane as the ion-associations Rh (Pd, Pt)-$SnCl_3$-diantipyrylmethane	Pd and Pt in spent autocatalyst were determined by the developed methods	[190]

and 2-mercaptobenzothiazole in 1.2 M HCl medium. This method used to analyse Pt and Rh in some metallurgical samples. Other reagents include $SnCl_2$ [226,227], sodium *p*-(mercaptoacetamide) benzenesulphonate [228] and meso-tetra(3-methoxy-4-hydroxyphenyl)porphine for the simultaneous determination of Rh and Pt [229]. In Table 5 give more reagents for determination of these elements.

Optimised partial least squares (OPLS), which introduces locally weighted and random matrix method into PLS for optimisation calibration model, can prevent the useful information from outflow and improve the precision of determination. The method applied to the simultaneously spectrophotometric determination of Rh, Ir and Pd in simulated geological samples [234]. The separation of trace noble metals in geological samples by cation exchange resin and simultaneous determination of Au, Pt, Pd and Rh with PLS regression spectrophotometry were studied by Chen et al. [235]. In addition, conditions of the colour reaction of Au, Rh and Pd with $SnCl_2$-rhodamine B-arabic gum studied by using PLS regression spectrophotometry [236]. Wang et al. [237] have proposed determination of trace Rh, Au, Pd and Ru in geological samples by solvent flotation-partial least squares regression-spectrophotometry. The optimum conditions of solvent flotation of trace noble metals and the colour system of metals-$SnCl_2$-rhodamine B studied. The PLS spectrophotometry was used to resolve the overlapping absorption spectra of the associated complexes.

The overlapping spectra of the multicomponent system of the noble metals in geological samples have been investigated by using the algorithm of the combined fuzzy cluster and PLS method. The optimisation of the calibration sets, for Au, Pt, Pd and Rh, in the calculation spectrophotometric analysis achieved and the precision of the results has been improved [238]. Table 5 shows other determinations.

Table 5
Simultaneous determination of Rh in the presence of other PGE

Mixtures	Reagents	Remarks	Reference
Rh, Ir	1-(2-Pyridylazo)-2-naphtol	Extraction with $CHCl_3$, the absorbances measured at 598 and 550 nm, respectively	[193]
Rh, Ir	$SnBr_2$, HBr and $HClO_4$	Extraction in isoamyl alcohol, determination of Ir in the aqueous phase	[194]
Rh, Ir	Pyridyl- and thiazolylphenols	Determination of Ir and Rh in glass and noble metal alloys	[195]
Rh, Ir	1-Phenyl-3-thiobenzoyl thiocarbamide	Extraction in $CHCl_3$, the maximum absorbance is at 435 and 425 nm, respectively	[196]
Rh, Ir	Pyridylazoresorcinol group	–	[197]
Rh, Ir	2-Pyridylazo-*p*-cresol, 2-thiazolylazo-*p*-cresol, 2-(2-thiazolylazo)-5-diethylaminophenol	At pH 5–6, in alloys, concentrates and synthetic mixtures, interferences were eliminated by using extraction and surfactants	[198]
Rh, Ir	1,5-Diphenylcarbazide	Sequential determination: Rh complex formed at 70 °C and extracted into isobutanol, Ir complex was then formed by heating for 45 min and measured in aqueous solution	[199]
Rh, Ir	3-Hydroxy-2-methyl-1,4-naphthoquinone 4-oxime	Optimum ranges: 0.27–5.24 and 1.51–15.85 g ml^{-1} over pH 5.0–7.5 and 5.3–8.0, respectively	[200]
Rh, Ir	Pyridylazoresorcinol group	Effect of microwave radiation on the complexation	[201]
Rh, Pd	Phthalimide dithiosemicarbazone	In slightly acid medium to form orange–red and yellow complexes, respectively, which have absorbance	[204]
Rh, Pd	Eriochrome cyanine R in the presence of cetylpyridinium	A column of Amberlite IRC 50 (Na^+ form) ion exchanger and the effluent was applied to a column of Dowex 2 resin	[205]
Rh, Pd	–	In nuclear reactor fuel reprocessing solutions	[206]
Rh, Pd	NaN_3	λ_{max} = 397 nm, Pd-complex formed instantaneously, while Rh-complex formation increased with time, by measuring the total absorbance with time	[207]
Rh, Pd	Phenanthrenequinone monosemicarbazone	At 480 and 470 nm, pH 7.2–8.8 and 5.0–7.0, respectively	[208]
Rh, Pd	4-(2-Thiazolylazo) resorcinol in presence of cation-active tensides	Binary complex Rh: pH 5.0, 520 nm Ion-association Rh: pH 5.6, 545 nm Ion-association Pd: pH 5.0, 540 nm	[209]
Rh, Pd	Pd: sulfonitrazo E Rh: sulfoallthiox	Pd: at 555 nm in H_2SO_4-H_3PO_4 Rh: at 450 nm in H_2SO_4, ascorbic acid	[210]
Rh, Pd	1-Mercaptopropionic acid *p*-phenetidide	Extraction with $CHCl_3$, at 375 and 410 nm, respectively	[211]
Rh, Pd	Bis(thiophene-2-aldehyde) thiocarbohydrazone	λ_{max} = 390 nm, extraction with ethyl acetate, pH 2.2–5.0 and 4.8–5.9, respectively	[212]
Rh, Pd	2-(5-Bromo-2-thiazolylazo)-5-dimethylaminobenzoic acid	pH 4.0, Pd reacts after 30 min at room temperature (λ_{max} = 685 nm), Rh reacts by heating in boiling water bath for 5 min (λ_{max} = 678 nm)	[213]
Rh, Pd	2-(2-Thiazolylazo)-5-dimethylaminobenzoic acid	pH 4.5, absorption maxima are 516, 682 and 674 nm for Pd and 586, 683 and 675 nm for Rh	[214]
Rh, Pd	Difurfurylthiocarbohydrazone	In alloys and synthetic mixtures, Pd-complex at room temperature, Rh-complex by heating in boiling water-bath for 15–20 min, λ_{max} = 377 nm	[215,216]
Rh, Pd	*N*,*N*′-dipyridylthiourea	335 and 330 nm, respectively	[217]
Rh, Pd	Bis(indole-3-aldehyde) thiocarbohydrazone	Extraction, at 385 nm	[218]
Rh, Pd	2-(3,5-Dichloro-2-pyridylazo)-5-dimethylaminoaniline	In HAc–NaAc media, on-line microwave FIA technique	[219]
Rh, Pd	Pyrazoldithiocarboxylic acid	Rh: pH 5.0–5.8, 414 nm Pd: pH 8.4–9.8, 428 nm	[220]
Rh, Pd	5-(5-Nitro-2-pyridylazo)-5-dimethylaminoaniline	Rh: pH 3.5–7.0, red complex, Pd: blue complex in a strong acidic medium, in ore and catalyst	[221]
Rh, Pd	2-(5-Nitro-2-pyridylazo)-5-dimethylaminoaniline	Double-wavelength overlapping spectrophotometry	[222]

Table 5 (*Continued*)

Mixtures	Reagents	Remarks	Reference
Rh, Pd	5-Br-PADAP	By resin spectrophotometry	[223]
Rh, Pt	Chromazurol S	In presence of cation-active tensides	[230]
Rh, Pt	$SnCl_2$	Dual-wavelength spectrophotometry	[231]
Rh, Pt	2-Methyl-1,4-naphthoquinone monoxime	Rh: golden yellow, 420 nm	[232]
		Pd: yellow, 430 nm	
Rh, Re	–	In catalysts after preliminary separation based on the solubility of heptavalent Re salts and the insolubility of Rh salts in ammonium, at 403 nm for Re and 475 nm for Rh	[233]
Rh, Pd, Ru	Monobenzoylthiourea	Extraction with $CHCl_3$, Pd from 0.25 to 8.0 M HCl, Rh at pH 4.4–5.6, Ru at pH 4.0–6.4	[239]
Rh, Os, Pd	Thiotropolone	Pd in cold, Rh and Os heated on a boiling water bath	[240]
Rh, Ir, Pt	$SnCl_2$, SnI_2 and rubeanic acid, respectively	Pt: extraction in Bu_3PO_4, 510 nm; Rh: 475 nm; Ir: 446 nm	[241]
Rh, Pd, Pt	Pt and Pd: dibenzyldithio-oxamide-potassium iodide-ascorbic acid	Pt and Pd: double wavelength	[242]
	Rh: $SnBr_2$, 2-mercaptobenzothiazole	Rh: Extraction	
		In automobile exhaust-gas purifying catalysts	
Rh, Au, Ir, Pd, Pt	Pd: α-furildioxime	Pd: extraction in $CHCl_3$, at 380 nm	[243]
	Au: rhodamine B	Au: extraction in isopropanol, at 555 nm	
	Pt: rubeanic acid	Pt: extraction in Bu_3PO_4, at 510 nm	
	Rh: $SnCl_2$	Rh: extraction in Bu_3PO_4,	
Rh, Ir, Pd, Pt	Various reagents	Solvent extraction separation in successive steps	[244]

6. Conclusions

Despite being regarded by many analysts as obsolete, spectrophotometry still enjoys great popularity, which seems to be increasing in some fields. Atomic absorption and inductively coupled plasma emission and mass spectrometry, rapidly developed during the past two decades, have diminished the role of spectrophotometry as the routine analytical technique in many laboratories. The low detection limits and enhanced selectivity of atomic spectrometric techniques together with the use of sequential multi-element determination capabilities makes these techniques better suited than spectrophotometry. However, the latter technique continues to be widely popular in view of their speed, simplicity, precision, accuracy and common availability of the instrumentation.

Advances in the synthesis of new organic reagents will occur, but whether they will be able to bring about a breakthrough in analytical spectrophotometry is rather doubtful. Examination of various mixed ligand ternary and multicomponent systems, developed over the last decades, indicates there is little scope in the future as they are unlikely to surpass in sensitivity over ion-association and surfactant sensitized systems. The use of multicomponent systems in surfactant-sensitized procedures is finding increasing attention over the last years. This trend is likely to continue in improving the sensitivity and selectivity of surfactant-sensitized procedures. Flotation spectrophotometric procedures developed over the last decades are mainly for noble metals, in view of their superior sensitivity. There is a shift in ion-association procedures over the last 20 years in the development of rapid, reliable, selective and sensitive aqueous procedures in place of extractive spectrophotometric procedures. This trend will continue with an emphasis on the application of developed procedures to real samples and in analysis of reference materials. Derivative and FIA spectrophotometric procedures are emerging areas where we will see many developments in the future. However, growing interest in automatic sample processing can place spectrophotometry as a detection technique due to the relatively low cost of the equipment and above all its far easier and cheaper maintenance. The drawback of poor selectivity is frequently overcome by powerful signal processing techniques. These all make spectrophotmetry a competitive technique, if not in ultra trace, at least in trace analysis.

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