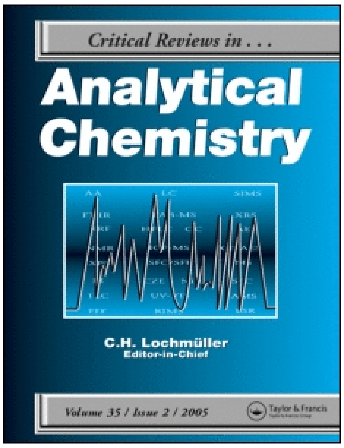

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Analytical Methods for the Determination of Ruthenium: The State of the Art

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I. INTRODUCTION

Ruthenium is a member of platinum group metals (PGM). The group consists of Ru, Rh, Pd, Os, Ir and Pt. The terms “noble” and “precious” metals are used to cover PGM and Au. Noble metals often occur together in natural samples.[1–4] Native metals or minerals usually contain small amounts of the other PGM accompanying the main components.

Unique physical and chemical properties of noble metals such as exceptional stability, hardness, malleability, electrical resistance, inertness to chemical attacks and excellent catalytic activity have resulted in their wide applications, *e.g.*, as catalysts in various chemical processes, in auto-catalysts, in electrical and electronic industry, in jewellery and others. Low abundance of precious metals, high economic value, large variety and complexity of materials to be examined have generated extensive research on methods for the determination of metals with satisfactory sensitivity, selectivity and reliability.[5] Complex chemical properties of PGM cause essential difficulties in developing reliable analytical procedures for their determination in various matrices. Close chemical similarity of particular metals provides necessity of their mutual separation prior to the detection by majority of available analytical techniques.

Ruthenium is the element of extremely complex chemical properties. Resistance to chemical attacks, the complexity of species in solutions, tendency to hydrolysis and formation of polynuclear forms, slow rate of reactions and numerous interfering effects from the other PGM present a serious challenge to develop reliable analytical procedures for its determination.

The state of the art of analytical methods developed for the determination of ruthenium in various materials is presented in the paper. Physical and chemical properties of the metal are described. Special attention is given to characterize ruthenium species in mineral acid solutions making the basis of majority of analytical procedures developed. Digestion methods that can be applied for quantitative transformation of ruthenium into soluble complexes are described.

Separation procedures (volatilization, coprecipitation, solvent extraction, sorption and chromatography) that can be used to isolate and to preconcentrate ruthenium from multicomponent samples, containing noble and base metals, are discussed. The applications of gravimetric and titrimetric methods, UV-VIS spectrophotometry, atomic absorption spectrometry (AAS), atomic emission spectrometry (AES), inductively coupled plasma mass spectrometry (ICP MS), X-ray fluorescence (XRF), neutron activation analysis (NAA), kinetic catalytic methods and electrochemical techniques to the detection of ruthenium at various concentration levels and in various materials are critically reviewed.

A. Discovery and Occurrence

Ruthenium (Ru, Z = 44, $4d^75s^1$, atomic weight 101.07) is the first element of a lighter triad of platinum group metals. The metal was discovered in 1844 by Karl Karlovich Klaus, Professor of Chemistry at the University of Kazan, Russia. Klaus examined the residues obtained after treatment of platinum ore with *aqua regia*. After fusing the residues with potassium nitrate and separation of osmium by distillation of volatile tetroxide he precipitated ammonium chlororuthenate under treatment with ammonium chloride. The name “ruthenium” given by Klaus has its roots in Ruthenia, the Latin name of Russia. Earlier, the discovery of *ruthen* in platinum ore was reported by Osann in 1827. It was not, however, confirmed by Berzelius who examined the same ore samples.

Ruthenium occurs in the Earth’s crust with the average abundances at 0.001 ppm.[3] It is associated with the other noble metals in their deposits. Iridiosmium (7 to 15% Ru), osmiridium (9 to 14% Ru), and laurite $(RuOs)S_2$ (65 to 67% Ru) are the major sources of ruthenium. Small quantities of ruthenium have been found in meteorites.

After isolating from the associated elements ruthenium can be obtained as metal powder (99.90 to 99.95%), the dioxide (RuO_2) and various halides.

B. Uses

Resistance to chemical attack, high catalytic activity and stable electrical properties decide of wide applications of ruthenium. The major uses of ruthenium are in electronics, electrical and electrochemical industries.[2] Chip resistors, resistor networks containing ruthenium thick film pastes and electrodes coated with ruthenium dioxide provide the main examples of its industrial applications. Ruthenium is a very effective hardener of platinum and palladium. Ru-Pt alloys containing up to 14% Ru are applied for electrical contacts. Alloys of high ruthenium content (30 to 70% Ru) containing the other platinum metals or some base metals are used for severe wear and corrosion resistance applications.

Elemental ruthenium, as well as a large number of its complexes, are widely applied as specific catalysts in chemical, petroleum and pharmaceutical industries. Distinguished chemisorption properties of ruthenium make it a very effective catalyst, *e.g.,* in Fischer-Tropsch synthesis. Recently ruthenium catalysts supported on active carbon have been found as very effective for ammonia synthesis.[2,6] Ruthenium (up to 5% Ru) is used to promote catalytic activity of platinum in electrochemical processes, *e.g.* in electro-oxidation reaction of methanol applied in fuel cells.[7,8] Oxoruthenium complexes have found to be particularly efficient for the mild and selective oxidation of alcohols.[9,10]

Recent investigations of ruthenium complexes as potential anti-cancer drugs promising to be alternative to platinum complexes already applied, are of special interest. Ruthenium red, $[(NH_3)_5Ru\text{-}O\text{-}(NH_3)_4Ru\text{-}O\text{-}Ru(NH_3)_5]Cl_6$; *cis*-tetraaminedichlororuthenium(III) chloride (*cis*-$[Ru(NH_3)_4Cl_2]Cl$); ruthenium dimethylsulfoxide (DMSO) complexes, such as *cis*- and *trans*-dichlorotetrakis(dimethylsulfoxide)-ruthenium(II) (*cis*- and *trans*-$[RuCl_2(DMSO)_4]$) and Na *trans*-$[RuCl_4(DMSO)(im)]$ (im = imidazol); HL *trans*-$[RuL_4Cl_2]$, (L is a *N*-heterocycle like indazole (in) or imidazole) have been recognized as highly active against some tumors with side effects lower than those from cisplatin.[2,11–16] Ruthenium(III)-complexes: imidazolium *trans*-[tetrachlorobis(imidazole)-ruthenate(III), HIm *trans*-$[RuCl_4(im)_2]$ and indazolium *trans*-[tetrachlorobis(indazole))-ruthenate(III), HIn *trans*-$[RuCl_4(ind)_2]$ exhibited the best results in antitumor tests. Recent studies on their interaction with serum proteins and reactions taking place in the cell (redox reactions, binding toward DNA, RNA and other target molecules) have been presented.[15,16]

The chemiluminescent activity of *tris*(2,2'-bipyridyl)ruthenium(II), $[(Ru(bipy)_3{}^{2+})]^*$, which is the product of reaction of *tris*(2,2'-bipyridyl)ruthenium(III), ($Ru(bipy)_3{}^{3+}$), with various substances, in particular of biological activity, makes the basis of sensitive and selective methods for the determination of a number of analytes, *e.g.*, oxalate and organic acids, aliphatic and cyclic amines, amino acids and proteins, pharmaceuticals and for immunoassay and DNA probe assay.[17–24] The $Ru(bipy)_3{}^{3+}$ electrogenerated chemiluminescence has been successfully coupled with capillary electrophoresis (CE) as a detection technique for amines and amino acids.[19] Luminescent $Ru(phen)_3{}^{2+}$ complex and its derivatives have also found applications as analytical reagents, *e.g.,* for the determination of oxalic[25] and nucleic[26,27] acids as well as pH sensors owing to pH-sensitive luminescence characteristics.[28] Recent application of piezoelectric Ru(III)/cryptand-coated quartz crystal gas chromatographic detector for olefins can be noted.[29]

C. Physical and Chemical Properties

Ruthenium is a dark-grey metal occurring in four crystal modifications: $\alpha \xrightarrow{1030-1040^0C} \beta \xrightarrow{1200^0C} \gamma \xrightarrow{ca.1500^0C} \delta$.[1] It has seven naturally occurring isotopes: ^{96}Ru, ^{98}Ru, ^{99}Ru, ^{100}Ru, ^{101}Ru, ^{102}Ru and ^{104}Ru with the relative abundance of 5.5%, 1.9%, 12.7%, 12.6%, 17.1%, 31.6% and 18.6%, respectively. High melting point (2310^{0}C) and hardness (6.5 in Mho's scale) are remarkable properties of the metal. Ruthenium is hexagonal in the crystalline state.

Metallic ruthenium is insoluble in mineral acids, including *aqua regia*. It can be converted into chloride complexes, widely used in analytical procedures, by alkaline oxidizing fusion of powdered metal with sodium hydroxide and sodium peroxide followed by acidifying the obtained ruthenate, RuO_4^{2-}, with hydrochloric acid.

Ruthenium undergoes oxygen attack at about 600^{0}C, with the formation of protective dioxide film which prevents the further oxidation. The volatile tetroxide RuO_4 is the best known ruthenium oxide. It is formed under the action of strong oxidizing agents, such as $HClO_4 + H_2SO_4$, HIO_4, $KMnO_4$, and Ce(IV) on the acidified solutions of ruthenium. Ruthenium tetroxide forms pale yellow crystals with a high vapour pressure at room temperature. It melts at 25.5^{0}C. RuO_4 is moderately soluble in water (2.03 g per 100 g H_2O at 20^{0}C) and very well soluble in carbon tetrachloride. A great care with its handling is required due to high volatility (b.p. 40^{0}C), toxicity and irritiant effect on the eyes.

Fluorine and chlorine attack ruthenium at higher temperatures (300 to 700^{0}C) yielding a number of binary fluorides and chlorides. Under heating ruthenium reacts with sulphur, selenium, tellurium and phosphorus. The prolonged action of hydrogen sulphide on the $RuCl_3$ solution results in the formation of yellowish-brown crystals of RuS_2. The ternary RuAsS, RuAsSe, RuAsTe, RuSbS, RuSbSe and RuSbTe compounds have been obtained.

Ruthenium occurs in its compounds in ten oxidation states, from -II to +VIII.[1] The II, III, IV and VIII are the most common oxidation states. Ruthenium exhibits close chemical similarity to osmium, the first element of the other triad of PGM. The octavalency of both elements (RuO_4, OsO_4) is unique in the periodic table.

Ruthenium(VIII) is represented only by the tetroxide, RuO_4. Ruthenium tetroxide is less stable than OsO_4, but it is more powerful oxidant. Ru(VII) occurs in the perruthenates RuO_4^-, easily reduced in alkaline solutions to ruthenates RuO_4^{2-}. Ruthenates and small number of the other compounds (RuF_6, $RuOF_4$, K_2RuF_6 and $Cs_2RuO_2Cl_4$) represent Ru(VI). The simple RuF_5 and fluororuthenate(V) complexes are the only examples of Ru(V) compounds. Ruthenium(IV) forms numerous halide complexes of the type of RuX_6^{2-} ($X = F^-$, Cl^-, Br^-) and $Ru_2OX_{10}^{4-}$ ($X = Cl^-$, Br^-). It occurs in ruthenites RuO_3^{2-} and in complexes with oxalate, sulphate, cyanide and nitrogen heterocycles ligands. Ru(IV) is easily reduced to Ru(III) which is the most stable oxidation state of the element. Ruthenium(III) forms a large number of complexes with halides, hydroxides, carboxylates, sulphides, ammonia, amines and nitrogen heterocycles, tertiary phosphines and arsines, CO and cyclopentadienyl ligands. Ruthenium is reduced from higher oxidation states to Ru(II) and an appropriate complex with ligands involved (*e.g.*, with $SnCl_3^-$ groups under the action of tin(II) chloride on acidified solutions of ruthenium) is formed. Complexes of Ru(II) with Cl^-, CN^-, NH_3, ethylenediamine (en), *N*-heterocycles and tertiary phosphine, arsine and stibine are known. A large number of nitrosyl complexes of Ru(II) distinguishes ruthenium among the other platinum metals. Carbonyl, cyclopentadienyl and hydride complexes of Ru(II), mostly of the type of RuH_xL_y (L = CO, halides, cyclopentadienyl, phosphine), are numerous. Carbonyl halide, $(RuCOBr)_2$ and $[Ru(CO)_xI]_n$, cyclopentadienyl and nitrosyl halide, $(RuNOX_2)_n$ ($X = Br^-, I^-$), complexes of Ru(I) are known. Ru(0) exists in carbonyl and carbonylphosphine complexes. The compound of Ru(-II), $H_2Ru(CO)_4$, formed under the treatment of $Ru_3(CO)_{12}$ with sodium in liquid ammonia followed by the action of phosphoric acid was reported.[30] Detailed characteristics of various complexes of ruthenium formed at different oxidation states were given.[1,31]

D. Complexes in Mineral Acids

High resistance of ruthenium to chemical attack, the complexity of species in solutions, their tendency for hydrolysis and formation of polynuclear complexes, slow rate of reactions and numerous interfering effects from the other platinum metals, in particular from osmium, present a serious challenge to develop and utilise the methods for the determination of ruthenium in various matrices. Chemical and instrumental methods generally require pretreatment steps ensuring quantitative conversion of ruthenium into suitable soluble complexes, separation of the analyte from the interfering elements and pre-concentration up to the level detected by the analytical technique employed. The availability of sample solution suitable for the analytical procedure used is essential. Hydrochloric, sulphuric, nitric and perchloric acid media are mostly applied in separation and determination methods. Chloride complexes make the basis of majority of developed methods. Quantitative conversion of ruthenium into stable complex of definite composition is required, in particular prior to chemical determination methods such as liquid chromatography and spectrophotometry. Deep knowledge on chemical behaviour of ruthenium in various media is essential for appropriate interpretation of the obtained results.

Complexes in hydrochloric acid. Ruthenium in hydrochloric acid can exist at VI, IV, III, and II oxidation states. The composition and stability of the complexes formed varies depending on the sample preparation procedure, HCl concentration, temperature and the age of the solution. All chloride complexes of ruthenium readily undergo hydrolysis in diluted (< 3 to 4 *M*) hydrochloric acid. A large number of hydroxo- and aqua-chlorocomplexes can be formed. The chemistry of chloride solutions of ruthenium, the equilibrium between various complexes formed and kinetics of ligand substitution reactions have been investigated by many authors.[32–56]

The complexes being the products of the reduction of RuO_4 in hydrochloric acid are of special interest. Hydrochloric acid is a very good absorption medium for the volatile tetroxide, mostly involved in separation procedures. Ruthenium(VIII) is easily reduced in HCl to lower oxidation states. The reduction rate and the type of the complexes formed depend on the HCl concentration, temperature and reaction time.[42,47,55] In 1 to 2 *M* HCl Ru(VIII) passes into Ru(VI) complex $RuO_2Cl_4^{2-}$. The complex is not stable, further reduction to Ru(IV) with the formation of $RuOHCl_5^{2-}$ complex precedes slowly. Intermediate product, being probably a mixture of Ru(VI) and Ru(IV) exists in 3 to 4 *M* HCl. In 6 to 10 *M* HCl RuO_4 is quantitatively reduced to Ru(IV) and the $RuCl_6^{2-}$ complex is formed. The maximum stability of $RuCl_6^{2-}$ complex was observed in 8 *M* HCl.[55] No changes in the solution of the complex were observed within 24 h. The stability of the complex decreases with increase in HCl concentration. Slow partial reduction of Ru(IV) to Ru(III) in 9 to 10 *M* HCl (9% and 11% decreasing in maximum absorbance, respectively, within 24 h) and the formation of $RuCl_6^{3-}$ complex have been observed. The reduction is faster under heating the solution. Chloride complexes of Ru(III) are the products of the reduction of RuO_4 in hydrochloric acid solution containing ethanol.[45] The $RuH_2OCl_5^{2-}$ complex exibits the highest stability. The oxidation of the latter complex to Ru(IV) in the presence of perchloric acid and the composition of species formed were investigated.[44] It has been shown that various oxo, aqua and chloro complexes are formed in the medium of $HCl\text{-}HClO_4$. The $RuCl_6^{2-}$ complex was stabilized in the 2.8 to 3.9 HCl concentration range.

The complex of Ru(IV) μ-oxo-bis(pentachlororuthenate), $Ru_2OCl_{10}^{4-}$, is the product of absorption of RuO_4 in water followed by acidifying of the obtained solution with 3 to 6 *M* HCl.[36,43] The complex is considered to be the most stable among chloride complexes of Ru(IV). Saturation of its solution with KCl leads to precipitation of the $K_4Ru_2OCl_{10}$ salt. Binuclear complex of Ru(IV) was also identified as a product of slow hydrolysis of $RuCl_6^{2-}$ complex in 2 *M* HCl.[33,37] In diluted hydrochloric acid (0.1 to 1 *M*) both complexes, $RuCl_6^{2-}$ and $Ru_2OCl_{10}^{4-}$, undergo hydrolysis. The $[Ru(OH)_2Cl_x(OH)_y(H_2O)_{8\text{-}x\text{-}y}]^{6-x-y}$ complex was described as the final hydrolysis product.[41] The reduction of binuclear $Ru_2OCl_8(H_2O)_2^{2-}$ complex, identified in 1 to 2 HCl, was investigated.[54] Various ruthenium chloro complexes, $RuCl_6^{2-}$, $RuH_2OCl_5^{-}$, $RuOHCl_5^{2-}$ and $Ru_2OCl_{10\text{-}n}(H_2O)_n]^{(4-n)-}$ (n = 1 or 2), co-existing in solutions owing to hydration, hydrolysis and polymeric reactions were described.[56] It was suggested that freshly prepared $RuCl_6^{2-}$ complex passes in diluted HCl (from 1 *M* HCl to pH 4 (buffer medium)) into $RuH_2OCl_5^{2-}$ gradually transformed into $RuOHCl_5^{2-}$ and dimeric hydrated ruthenium chloro anion $[Ru_2OCl_{10\text{-}n}(H_2O)_n]^{(4-n)-}$.

The $RuOHCl_5^{2-}$ and $Ru_2OCl_{10}^{4-}$ complexes were found to be the products of acidifying ruthenate solutions obtained after alkaline oxidation fusion of metallic ruthenium.[48] The $RuOHCl_5^{2-}$ complex predominated in 1 to 2 *M* HCl. The increase in HCl concentration up to 6 to 10 *M* HCl results in the formation of binuclear form. The equilibrium between these two complexes was established. The $RuOHCl_5^{2-}$ complex was also the final product of the reduction of RuO_4 in 4 to 5 *M* NaOH followed by acidifying with 1 *M* HCl. Ruthenium as $RuCl_6^{2-}$ was detected in 6 *M* HCl.

Chloride complexes of Ru(IV) formed in perchlorate solutions while adding chloride ions were studied.[32,35,39,40,51] The evidence of the complexes: $Ru(H_2O)_2(OH)_2Cl_2$ (violet complex), $RuH_2O(OH)_2Cl_3^{-}$ and $Ru(OH)_2Cl_4^{-}$ (yellow complexes) was provided. The effect of ionic strength and the concentration of chloride ions on the kinetics of transformation between various complexes were studied. It was found that the rate of substitution of aqua ligands by chloride ions increased with the following changes in ionic composition $H^+ > Li^+ > Na^+$.[39,51] Ruthenium perchloride solution can be obtained by the reduction of RuO_4 in $HClO_4$ in the presence of H_2O_2.[35]

In aqueous-methanollic solutions: 1 *M* $HClO_4$-1 *M* HCl-(Ru(IV) as $Ru_2OCl_{10}^{4-}$)-90% $CH_3OH\text{-}H_2O$ the transformation of binuclear complex into $Ru_2Cl_6(CH_3OH)(H_2O)(OH)_2$ species was suggested.[46] The stability of binuclear structure in 5 *M* H_2SO_4 was examined.[52] Aquation of $Ru_2OCl_{10}^{4-}$ complex anion to $Ru_2OCl_8(H_2O)_2^{2-}$ and further substitution of three chloride ions in coordination sphere of each metal atoms were reported.

The nature of Ru(III) species existing in various media, equilibrium between various complexes formed and kinetics of the ion exchange reactions were investigated.[34,38,49,50,53] It has been found that the composition of the complexes formed is largely affected by HCl concentration. Anionic complexes of Ru(III) are labile to substitution and equilibrate rapidly in solutions. The $[RuCl_4(H_2O)_2]^-$, $RuCl_3(H_2O)_3$, $[RuCl_2(H_2O)_4]^+$ and $RuCl(H_2O)_5]^{2+}$ species were identified in solutions obtained after dissolution of $RuCl_3 \cdot 3H_2O$ in 0.1 *M* KCl at pH 0.4, 1.0 and 2.0 at temperature 25^0C.[49] The $[RuCl_2(H_2O)_4]^+$ complex was found the most stable under the conditions used. Conversion of the other forms into the latter complex was established. The conversion was fast in solutions heated to temperature 70^0C at pH 2.0. The initial concentration of particular species, as well as HCl and KCl concentrations, affect kinetics of aquation of $[RuCl_4(H_2O)_2]^-$, $RuCl_3(H_2O)_3$, $[RuCl_2(H_2O)_4]^+$ and $RuCl(H_2O)_5]^{2+}$ complexes.[50] The existence of two cationic, $RuCl^{2+}$ and $RuCl_2^+$, and neutral $RuCl_3$ species in solutions was reported.[34] The experiments on kinetics of ligand substitution in Ru(III) ($RuCl_6^{3-}$), Ru(IV) (a mixture of $RuCl_6^{2-}$ and $RuOHCl_5^{2-}$) and Ru(II) ($RuCl_4^{2-}$) complexes in 11 *M* HCl at temp. 25^0C using $^{36}Cl^-$ isotope were carried out.[38] It was revealed that the ligand lability decreased in the order of Ru(II) > Ru(III) > Ru(IV) complexes. The introduction of ethanol into $RuCl_3$ solutions leads to the formation of cationic, neutral, and anionic species in which water molecules are substituted by ethanol.[53] The disproportionation of these species to Ru(0) and $RuO_2 \cdot xH_2O$ can occur. The binuclear, neutral $(RuOH)_2Cl_6H_2O$ form was identified directly after dissolution of $RuCl_3 \cdot xH_2O$ in ethanol under the open air. The intermediate reduction product containing Ru(IV,III) in the $(RuOH)_2$ group was identified.

Complexes in sulfuric acid. Numerous complex sulphate species of ruthenium of high tendency for hydrolysis and formation of polynuclear forms have been identified in sulphuric acid media.[57–67] The composition of the sulphate complexes varies depending on the kind of ruthenium complex reacting with sulfate ligands, the concentration of sulfuric acid, temperature and reaction time.

The complexes formed under the interaction of RuO_4;[57–60] $Ru(OH)_4$, precipitated from alkaline solution of $K_4Ru_2OCl_{10}$, with SO_2[62] and $K_2RuH_2OCl_5$, $K_4Ru_2OCl_{10}$ and $Ru(OH)_4$ with H_2SO_4 of different concentrations[60,61] have been investigated. Dark brown precipitate, which was identified as the $Ru^{VI}O_2S_2O_7$ compound was a product of the reaction of RuO_4 with SO_2.[58] The compound was stable in dry air below 150^0C. The liberation of SO_3 was observed at higher temperature. Oxosulphate of Ru(IV), $RuOSO_4$, was found in solutions of $RuO_2S_2O_7$ in diluted sulfuric acid at room temperature. A green $RuO_2SO_4^{2-}$ complex anion was formed in the same solution at 0^0C. The hydrolysis of the $RuO_2S_2O_7$ complex followed by precipitation of hydrated dioxide, $RuO_2 \cdot xH_2O$, occurred in pure water solution. The conversion of Ru(IV)-hydroxide, precipitated from $K_4Ru_2OCl_{10}$ solution at pH 6.5, into soluble $[Ru(SO_3)_2(H_2O)_4]^-$ under the action of SO_2 was reported.[62]

The reaction of $RuO_2 \cdot xH_2O$, $K_4Ru_2OCl_{10}$ and $K_2RuH_2OCl_5$ with H_2SO_4 at 250 to 320^0C leads to the formation of the brown $K_4H_6[Ru_4O_6(SO_4)_6]$ complex containing ruthenium at mixed oxidation states (III and IV).[61] The green oxosulphate of Ru(IV), $K_8[Ru_3O(SO_4)_9]$, was identified as a product of fusion of the examined chlorides with hydrogen sulphate. The interaction of various binuclear complexes of ruthenium with potassium disulphate at 400^0C and crystal structure of the species formed were studied.[66] Green and brown sulphates were obtained earlier[60] under the action of conc. H_2SO_4 on Ru(IV) complexes at different temperatures, 150 to 180^0C and 250 to 300^0C, respectively. The existence of ruthenium at mixed (III,IV) oxidation states and the presence of O_2^{2-} or O_2^- groups in the examined complexes were suggested.

A hydrolytic conversion of two brown sulphates, $K_2H[Ru_2^{III,IV}O_2(SO_4)_3(H_2O)_2]$ and $K_6[Ru_3^{III,III,IV}O(SO_4)_6(HSO_4)_2H_2O]$, and a green $K_8[Ru_3O(SO_4)_9]$ complex into various cationic and neutral forms in 0.005 to 2 *M* H_2SO_4 was reported.[64] Studies of behavior of ruthenium sulphates, $K_4[Ru_4(SO_4)_6O_2(OH)_4]$, $K_2H[Ru_2(OH_2O)_2(SO_4)_3]$, $K_8[Ru_3O(SO_4)_8H_2O]$ and $K_8[Ru_3O(SO_4)_9]$ in a large sulfuric acid concentration range (0.05 to 18 *M*) at 25^0C and 75^0C were carried out.[63] The $K_8[Ru_3O(SO_4)_9]$ complex exhibited the greatest stability. All examined complexes are gradually converted into the $K_2H[Ru_2(OH_2O)_2(SO_4)_3]$ complex stable in 5 to 18 *M* H_2SO_4 and undergoing hydrolysis in diluted (0.05 to 2 *M*) sulfuric acid.

It has been established that a kind of cation involving in the formation of the neutral ruthenium sulfates affects their final composition. The effect of Li^+, Na^+, K^+, Cs^+, Zn^{2+}, and Al^{3+} cations on the composition of the compounds of ruthenium formed at temperature 250 to 450^{0}C in argon and oxygen atmosphere was studied.[65] The conversion of green and brown sulfates into various forms under the action of reduction agents was investigated.[67]

Complexes in nitric acid. In nitric acid solutions ruthenium can exist in various nitroso nitrate complexes of Ru(III), $[RuNO(NO_3)_n(H_2O)_{5-n}]^{3-n}$ and $[RuNO(NO_3)_{5-n-m}OH_m(H_2O)_n]^{p-}$, or polymeric hydroxo nitrates of Ru(IV), $[Ru(OH)_x(H_2O)_{6-x}](NO_3)_{4-x}$.[42] Nitroso complexes are more stable in comparison with pure nitrates.

All nitroso nitrate complexes of ruthenium easily undergo hydrolysis.[68,69] Different products depending on pH of the examined solution, temperature and reaction time can be formed. Slow transformation of hydrolytic products into polymeric forms can occur. Sparingly soluble products precipitate at higher temperature. The precipitation of $RuNO(OH)_3$ at pH 5 to 8 was reported. The precipitate dissolves above pH 8.5.

The $RuNO(NO_3)_3{\cdot}4H_2O$ was isolated from the solutions of RuO_4 in HNO_3 treated with nitric oxide and evaporated in vacuum at room temperature.[70] In solutions, various anionic and cationic forms were identified.

The mixed nitroso nitrite $[RuNO(NO_2)_4OH]^{2-}$ complex is formed under the treatment of chlorides, nitroso chlorides and nitroso nitrates with an excess of KNO_2. The complex was considered to be more stable in aqueous solutions.[69] In HNO_3, $HClO_4$ or HCl partial substitution of NO_2^- groups by H_2O or Cl^- ligands can occur. The $[RuNO(NO_2)_2(H_2O)_2OH]$ complex was identified in HNO_3 and $HClO_4$ solution. Instability of some nitrosyl ruthenium compounds in nitric acid was investigated.[71,72]

II. SAMPLE PREPARATION

A. Digestion Methods

A great resistance of ruthenium to chemical attack makes its quantitative transformation into soluble species a challenge. Alkaline oxidizing fusion and chlorination are, among the methods applied to the decomposition of noble metal samples,[42,73] the most effective for quantitative conversion of ruthenium into soluble complexes.

Pure ruthenium resists mineral acids attack (including *aqua regia*). The metal can be transformed into the solution under wet acids treatment when accompanies (up to 5%) platinum and palladium, *e.g.,* in platinum- and palladium-base alloys.[74,75] If a small insoluble residue remains it can be solubilized by alkaline oxidizing fusion. The combination of acids (HF-*aqua regia*) digestion with alkaline fusion was successfully applied to the determination of ruthenium and the other noble metals in geological materials.[76,77] Micro- and nanogram amounts of Ru (Rh, Pt, Ir, Pd, Ag and Au) in silicate rocks, ores and metallurgical samples were determined by employing HF-*aqua regia* attack.[78] The 20 to 40%[79] and 30%[80] recoveries of Ru and the other PGM were reported using *aqua regia* leach of the analytes from geological samples of ophiolitic origin, including chromitites, in conventional teflon vessel and from ore samples under microwave heating, respectively. The application of Carius Tube for acids digestion of geological samples, minerals, metals and sulfides with extremely low PGM contents has been described recently.[81–83] The method provides low procedural blanks (1 to 15 pg g^{-1} level for Ru, Pd, Ir and Pt[83]). The DL of 5 pg g^{-1} Ru in geological samples was reported.[81]

Finally, powdered ruthenium, ruthenium oxides, and insoluble salts are readily attacked by alkaline hydroxides in the presence of oxidizing agent. Sodium peroxide alone or mixed with NaOH are most frequently used as a flux. Large amounts of salts and contaminations introduced to the sample (including those from the wall of crucible attacked by the flux) are disadvantages of fusion procedures. The application of the method is restricted to small sample weights. Silver crucibles are often used to perform a fusion procedure. Silver, which partially passes into the melt during the fusion operation, can be quantitatively removed in the form of AgCl after acidifying the melt with HCl. Nickel crucible can also be used successfully.

Ruthenium (up to *ca.* 30 mg) was completely oxidized to sodium ruthenate, Na_2RuO_4, under treatment with a mixture of NaOH + Na_2O_2 (1 g + 0.2 g) at 450 to 600^0C.[84] Fusion with sodium peroxide was used to decompose geological samples (0.5 g) containing Ru, Pd, Pt, and Ir.[85] Glassy carbon crucibles were used in fusion procedures. In order to protect the crucible from the sodium peroxide flux, a layer of sodium carbonate was applied to line the bottom and walls of the crucible before each fusion. Detection limit of 1 pg g^{-1} Ru in geological samples has been reported using a sodium peroxide digestion procedure.[86]

Ruthenium, as well as the other platinum metals, undergoes chlorine attack yielding binary chlorides and salts, both of each dissolved in hydrochloric acid.[73,87] Three types of chlorination procedure are used: “direct” chlorination in the presence of large amounts of an alkali chloride, “wet” chlorination at elevated temperatures and pressures in a sealed tube containing HCl and oxidizing agent, and “dry” chlorination by hot chlorine passing over the sample usually mixed with a small amount of NaCl in an open tube at 500 to 600^0C. Dry chlorination has some advantages such as low concentration of salts and low blank levels. Large samples that can be submitted for analysis and low level of contamination are essential.

Ruthenium(III), α-$RuCl_3$ and β-$RuCl_3$ (insoluble in water) and ruthenium(IV), $RuCl_4$, chlorides were identified as the products of chlorination procedure.[1,88] Solid β-$RuCl_3$ (soluble in alcohol) and gaseous $RuCl_4$ are formed at 430 to 510^0C. Above 580^0C β-$RuCl_3$ is converted into α-$RuCl_3$ (insoluble in alcohol), identified also in vapour over the solid phase. Gaseous $RuCl_3$ is the chlorination product at 840 to 920^0C. Chlorination of a mixture of ruthenium with NaCl at 450 to 580^0C gives the sodium ruthenate, Na_2RuCl_6.

Low concentrations (ng g^{-1}) of ruthenium and the other noble metals present as native metals, natural alloys and PGM (or Au) bearing sulfide group minerals in rock pulps were determined by dry chlorination with recoveries > 90%.[87] Analysis of three reference rock pulps showed that the dry chlorination method produced results comparable to, and often better than fire assay technique, widely used for digestion of noble metal samples.

The chlorination of ruthenium and the other PGM (at % levels) employing two closed systems: a mixture of HCl and $KMnO_4$ in autoclaves (at 160^0C) or carbon tetrachloride and cupric chloride in sealed ampules was examined.[89] The compositions of the products of chlorination at different temperatures were suggested.

The action of chlorine and hypochlorides in alkaline solution leads to the conversion of ruthenium into the volatile teroxide, RuO_4.[90] The procedure can be effectively applied to the isolation of ruthenium from the noble metal samples by distillation. Osmium, if present in the sample, is also oxidized to volatile OsO_4 and distills with ruthenium. The hydrolysis and formation of sparingly soluble hydrated oxide in saturated NaOCl solution can occur. Saturation with chlorine and intermittent additions of hydroxide may improve the recovery of ruthenium.

Classical fire assay involving the lead collection is a universally accepted method for the decomposition of noble metal samples.[73,75,91] The method involves a fusion of a sample at high temperature with a flux (Na_2CO_3, $Na_2B_4O_7$), reducing agent (flour, starch) and a collector (PbO). On fusion the analytes are extracted from a complex matrix into the resulting lead button formed. The matrix elements react with the flux component to form a slag that is subsequently discarded. The lead button is placed on a cupel prepared from bone ash or magnetite. On heating at the temperature about 800 to 850^0C in an oxidizing atmosphere the lead oxide and the non-noble metal oxides are produced and absorbed into the cupel where upon a bead of precious metals remains. The precious metals alloy is usually treated with mineral acids to extract the analytes.

The classical lead fire assay has found limited applications to the recovery of ruthenium, osmium and iridium from complex matrices, *e.g.,* from geological samples. Serious losses of ruthenium were reported.[92] Significant retention of the metal by the slag and the cupel occurred. Losses of ruthenium in the form of volatile tetroxide during the fusion and partial cuppelation were found to be negligible. The application of lead fire assay followed by a vacuum distillation of the lead matrix to simultaneous determination of all PGM and Au in a concentrate was described.[93] The determination of Ru and Ir (in the 5 ppb to 0.1 ppm concentration range) and Pt, Pd, Rh and Au (in the 0.5 ppb to 0.1 ppm concentration range) in products of complex composition was reported.[94] Different modifications of micro fire assay preconcentration using a Pb collector were applied to the determination of noble metals in ores.[95]

The other fire assay collectors: nickel sulphide, iron-nickel-copper alloys and tin have proved to be more effective to the determination of low levels of ruthenium and the other noble metals (in particular of Ir and Os). Nickel sulfide fire assay has gained the widest popularity.[96–110] The procedure is thought to be capable of quantitative concentration of all PGM on a nickel sulphide button obtained.

The NiS involves fusion of the sample with Ni, S, $Na_2B_4O_7$, Na_2CO_3 and SiO_2 in a clay crucible at temperature of *ca.* 1000^0C. The NiS bead formed is separated from the slag, than crushed and dissolved in conc. hydrochloric acid. The matrix elements are removed under HCl treatment. The insoluble precious metal sulphides are filtered and dissolved in HNO_3 and HCl. High procedural blank resulting from chemicals required for flux and sample preparation is the disadvantage of NiS fire assay method.

The effect of the collector mass on the recovery of PGM in analysis of geological samples (ore ($< \mu g\ g^{-1}$ PGM) and a komatiite ($< 10\ ng\ g^{-1}$)) was studied.[105] The recoveries of Ru (Rh, Pd, and Pt) in komatiite increased with increase of the collector mass. They were independent of the mass of the collector used in analysis of PGM ore reference material (SARM-7). Some losses of Ru, Os and Au[97,102] at the dissolution and filtration stage were reported. Bubbling hydrogen sulfide gas through the solution toward the end of the dissolution stage may minimize these losses. Detailed studies on the recovery and losses of PGM, including optimization of a button size and dissolution technique, were presented.[101]

The effects of various factors (composition of the flux, the relationship between the mass of mixture and sample, value of the Ni : S ratio, fusion time and temperature) on the effectiveness of the nickel sulphide fire assay concentration of noble metals were investigated.[106,108] The chemical composition of phases in button obtained using sodium tetraborate and lithium tetraborate as a flux was formulated.[107] Lithium tetraborate provided a lower recovery rate than sodium tetraborate, except for chromitites with PGM abundances in the ppm range. The highest recoveries were obtained for the 1 : 1 mixture of two tetraborates. Attempts to decompose ore samples containing noble metals (including Ru) under the action of fluorooxidants, BrF_3 and $KBrF_4$, have been described recently.[111]

Conversion of ruthenium into soluble species by electrochemical anode dissolution has been investigated.[112–114] Labile anionic and neutral oxoaquahydroxosulfate complexes of Ru(IV) were indentified in the electrolyte after anodic dissolution of Ni-Ru(1 to 10%) alloy in sulfuric acid solution.[112] The slime formed in the electrolysis was a finally dispersed product consisting of amorphous Ru metal and its oxides. The mixture of ruthenates and perruthenates free of larger amounts of another salts was obtained in alkaline (NaOH or KOH) media.[113] Standard solution of Ru(IV) of $1.6 \cdot 10^{-3}$ *M* in HCl was prepared by anodic dissolution of powdered metallic ruthenium.[114]

Stepwise dissolution of geological samples resulting in separation of particular components into eight phases (water-soluble phase, exchangeable phase, carbonate phase, Fe/Ni metal phase, sulphide phase, oxide phase, silicate phase and HF-insoluble residue) was proposed for the speciation of Ru (Rh, Pd, Ir, and Pt).[115] About 30% of Ru (similarly to Ir and Rh) were found in the metal phase, 25% in sulfide or residue phase and only 1 to 3% in a silicate phase. The dissolution procedure was combined with NiS FA to preconcentrate the analytes from particular components obtained.

B. Separation and Preconcentration Methods

1. Volatilization

Separation of ruthenium from multicomponent noble and base metal solutions is commonly accomplished by distillation of volatile tetroxide, RuO_4. Ruthenium passes into RuO_4 in the presence of strong oxidants such as $HClO_4 + H_2SO_4$, $NaBiO_3$, $K_2Cr_2O_7$, Cl_2 (in alkaline media) and $KMnO_4$.[42,47,55,73,74,116] The distillation at the temperature of 105 to 110^{0}C is an effective way for selective isolation of RuO_4 from complex matrices. Only osmium, if present in the sample, is also oxidized to OsO_4 and codistills. Partial volatilization of the other elements, Fe and Ir, Re, Se, Te, and Cr may occur at higher temperature, 150^{0}C and 220^{0}C, respectively.

Perchloric acid in the presence of the other mineral acid, mostly H_2SO_4, is one of the most efficient oxidant for ruthenium. Ruthenium is converted into RuO_4 under dense fumes of $HClO_4$. The oxidation of ruthenium to Ru(VIII) is also quantitative in the media of HCl, HBr, and H_3PO_4. Nitric acid should be removed from the sample prior to the oxidation. Nitroso complexes of ruthenium resist the quantitative conversion into RuO_4.[117] The distillation of ruthenium from perchloric acid medium is particularly convenient after preliminary digestion of the examined samples with the use of this acid. It was successfuly applied in analysis of Fe-Ni-Cu collection button from fire assay procedure.[118,119] Small amounts of $NaBiO_3$ introduced to the solution can be favorable, in particular when the concentration of $HClO_4$ is not sufficiently high. Ruthenium was also quantitatively volatilized from boiling sodium bismuthate-sulfuric acid slurry.[120]

Chlorine in alkaline media effectively oxidizes ruthenium to RuO_4 in the absence of iridium and rhodium. Hydrated oxides of iridium and rhodium precipitated from alkaline solutions can to some extent absorb ruthenium. Microgram amounts of ruthenium were converted into volatile tetroxide under treatment with permanganate.[74] Ruthenium quantitatively distills from the solutions of 0.1% $KMnO_4$ and 0.5 *M* H_2SO_4. The complete separation of RuO_4 from diluted permanganate usually requires longer time than the distillation from the media of concentrated mineral acids. It can allow however to avoid the contamination of the absorbing solution by acid decomposition products passing into the receivers. These products may interfere with further determination of the analyte by some analytical procedures.

Hydrochloric acid is a very good absorption medium for volatile RuO_4. Ru(VIII) is readily reduced in HCl to lower oxidation states with the formation of various chloride complexes, containing ruthenium in various oxidation states.[42,47,55] The reduction can be accelerated by the introduction of additional reductant (*e.g.,* $SnCl_2$, C_2H_5OH[45]) to hydrochloric acid solution. The distilled RuO_4 can also be quantitatively absorbed in alkaline hydroxide, *e.g.,* NaOH or KOH, solutions.[48,120] Ruthenium(VIII) is reduced to Ru(VII) in 1 to 2 *M* NaOH and Ru(VI) in 4 to 5 *M* NaOH. The RuO_4^- (perruthenate) and RuO_4^{2-} (ruthenate) anions are formed, respectively. Ruthenium passes into the $RuCl_6^{2-}$ complex after acidifying alkaline solutions of perruthenate and ruthenate up to 6 *M* HCl.

Osmium when passing into absorbing solution interferes with the detection of ruthenium by the majority of analytical methods due to high chemical similarity of the complexes formed by both elements in the examined media. Mutual separation of osmium and ruthenium is generally required prior to the detection. Easier oxidation of osmium than ruthenium to the tetroxide makes a basis of its preliminary separation from the examined samples. Osmium selectively distills from the solutions in the presence of weak oxidation agents, *e.g.,* H_2O_2 or dilute HNO_3.[74,117,121] Chlorides should be removed prior to the oxidation owing to high resistance of chloride complexes of osmium and ruthenium to quantitative conversion into tetroxides. The evaporation of the examined solution with sulfuric acid is favourable to remove chlorides.

The 3% H_2O_2 solution is often applied as absorption solution for both tetroxides. No losses of ruthenium were observed during boiling of the solutions of both elements in H_2O_2. Ruthenium can be converted into volatile RuO_4 and isolated from the samples under treatment with permanganate.[74]

Osmium can also be selectively separated from mixtures with ruthenium in nitric acid solution. A complete separation has found to be possible from the solutions of ≤ 5 *M* HNO_3. Slow and incomplete distillation is observed when osmium is present as either the chloro and bromo complexes. Volatilization of ruthenium from the media of higher nitric acid concentration was reported.[122] The presence of calcium phosphate significantly enhances the volatility of ruthenium.[123]

2. Precipitation

Precipitation methods are rarely used to isolate ruthenium from multi-component mixtures due to a lack of selective precipitants. Co-precipitation using suitable collectors makes the basis of analytical procedures for group separation of precious metals from matrix elements as well as their preconcentration.

Elemental tellurium obtained by *in situ* reduction using tin(II) chloride or NH_2OH has found the widest application as a collector for noble metals, including ruthenium. Co-precipitation with tellurium was effectively applied in analysis of geological materials after digestion of the samples by nickel-sulfide FA,[96,98,101,110,124,125] wet acids treatment[76] and sodium peroxide fusion.[85,86]

Thioorganic compounds such as thiourea, thioacetamid, thiophenol, β-thiopropionic acid and 2,3-dithiopropanol have been applied to preconcentrate ruthenium using copper sulfide as a carrier.[126,127] Ruthenium was effectively precipitated from nitric acid solutions in the presence of U, Pu, and other fission products by β-thiopropionic acid and 2,3-dithiopropanol.[128] Pressure precipitation of ruthenium with hydrogen sulfide was described for its separation from uranium.[129]

Trace amounts of ruthenium existing in the form of anionic complexes undergo association with large organic cations (*e.g.,* basic dyes) and precipitate as sparingly soluble adducts with simple salts of the dyes. They can be concentrated by solvent flotation methods.[130] The adducts are accumulated at the phase boundary or on the wall of separatory funnel while shaking an aqueous solution with a suitable non-polar organic solvent (*e.g.,* cyclohexane, toluene, xylene). Low selectivity of solvent flotation procedures is their disadvantage. The other noble metals interfere with the separation of ruthenium.

A co-precipitation of ruthenium from water samples with chitosan has been studied recently.[131] Ruthenium (0.1 to 5 :g) was quantitatively separated from the examined samples (100 to 1000 ml) at pH 7.5 to 8.5.

3. Solvent Extraction

Solvent extraction has been widely applied for separation and preconcentration of noble metals from their multicomponent mixtures as well as from associated base metals.[132,133] PGM species undergo extraction from aqueous solutions via a noncoordinating outer sphere mechanism under the action of neutral solvating agents (*e.g*., oxygen containing solvents, organophosphorous and neutral sulphur containing compounds) as well as in the form of ion-pairs, *e.g.,* with high-molecular-weight amines (R_3N) and quaternary ammonium salts (R_4N^+). Anionic complexes formed in halide and thiocyanate media make the basis of most extraction procedures for ruthenium. Chelate complexes with organic agents, *e.g.,* 8-hydroxyquinoline, carbamates, dithizone, and thiourea derivatives make the basis of numerous separation methods.

Differences in the kinetic rate of formation of extractable compounds as well as the strength of interaction of the analyte with solvating agents or liquid ion-exchangers allow the separation of ruthenium from mixtures with the other noble metals. It should be noted, however, that most of extraction separation procedures were developed for binary mixtures of ruthenium and osmium easily obtained by their simultaneous separation from the other noble metals by distillation in the form of the volatile tetroxides.

Separation of osmium and ruthenium by extraction of the tetroxides, OsO_4 and RuO_4, into inert organic solvents, *e.g.,* CCl_4 or $CHCl_3$, is considered as an alternative to their separation by distillation. Selective transformation of osmium into OsO_4 under treatment with weak oxidants followed by its extraction can precede the extraction of ruthenium. Special consideration should be given to the purity of the reagents used, in particular for quantitative extraction of RuO_4. Ruthenium tetroxide extremely easily undergoes reduction in the presence traces of contaminants or solvent decomposition products with the formation of nonextractable species. There are reports of 90 to 95% recoveries of ruthenium even in case of using specially purified carbon tetrachloride in extraction procedure.[134] Most often the extraction of both analytes is carried out from sulphate solutions obtained after evaporation of the examined samples with H_2SO_4 (until gentle fumes of the acid). Physical properties of OsO_4-CCl_4 and RuO_4-CCl_4 systems have been described.[135] The extraction of ruthenium into CCl_4 makes the basis of determining fission product Ru in neutron-irradiated plutonium[136] and separation of ^{103}Ru radionuclide from ^{103}Rh.[134,137]

The application of various complexing agents to convert ruthenium into stable extractable species that can be used in separation procedures has been widely investigated. Ruthenium can be separated from osmium[138–140] and rhodium[141] after conversion into thiocyanate complex. The extractability of ruthenium from thiocyanate media into variety of solvents was studied.[139] Cyclohexanone was reported as the best extracting agent from 0.8 *M* SCN^- and 1 *M* H_2SO_4 medium. Sequential extraction of thiocyanate complexes of osmium and ruthenium was used for the mutual separation of both metals. Ruthenium thiocyanate complex undergoes extraction by methyl isobuthyl ketone (MIBK) from 1 *M* HCl.[138] Osmium can be preliminary separated from the examined solution by extraction from 0.1 to 0.4 *M* HCl with diethyl ether containing small amounts of peroxide. High distribution coefficient (more than 10^4) was achieved while polyurethane foam was applied to extract ruthenium from thiocyanate media.[140,141] Advantages of the extraction of ruthenium and osmium using polyurethane foam over methods involving selective distillation of the tetroxides were discussed.[140] The separation of ruthenium from rhodium can be accomplished.[141] Rhodium is not extracted by polyurethane foam. It remains (*ca*. 95%) in the aqueous phase. Surfactant extraction of ruthenium from thiocyanate media into the Triton X-100 phase in the presence of Zephiramine has been investigated.[142] The other noble metals interfere with the extraction of ruthenium.

Ruthenium in the form of anionic complexes with chloride[143,144,145] and $SnCl_3^-$[114,146] ligands is effectively extracted by high-molecular-weight amines. Amine, usually dissolved in organic diluent, is transformed into organic cation (R_xNH^+) by reaction with acid present in aqueous solution. The cation reacts with anionic complex of the analyte existing in solution with the formation of the ion-pair, dissolved in the suitable organic solvent used as diluent. The other PGM existing in the examined sample in anionic forms can also be extracted. Systems using high-molecular-weight amines as extraction reagents allow to isolate the noble metals from common metals occurring as cations in acidic media. Extraction of ruthenium from thiocyanate media by *bis*-(2-ethylhexyl)amine was proposed for its determination in microelectronics materials.[147]

Thiourea and its derivatives were found to be the promising extraction agents for platinum metals.[148–152] The mutual separation of the analytes can be accomplished by choosing the suitable extraction parameters and variation in ligand structure. Extraction behaviour of ruthenium after complexation with *N,N*-dialkyl-*N′*-benzoylthioureas,[148–150] diphenylthiourea[151] and diantipyrylthiourea[152] has been investigated. The rate of extraction of Ru(III) with diphenylthiourea can be accelerated in the presence of $SnCl_2$ acting as labilizing agent. The separation and preconcentration of ruthenium from the solutions containing the excess of Ca(II), Mg(II), Ni(II), Cu(II), Al(III), Fe(III), and Co(II) using polyacrylacylisothiourea chelating fibre has been described.[153]

Chelates of ruthenium with quinoline-8-ol and its derivatives[154–157] make the basis of separation procedures. Extraction into molten naphthalene was effectively applied for separation of ruthenium from the samples of copper-nickel sulfide ores and concentrates.[155,157]

Ruthenium from copper-nickel ores was collectively extracted with the other noble metals by alkylaniline hydrochloride.[158,159] The method has been applied for extraction of Ru (Ir and Rh) from sulphate solutions.[159] Extraction of perruthenate, being the product of the oxidation of ruthenium by potassium periodate at pH 7.8, by benzyltributylammonium chloride in $CHCl_3$, was applied to the separation of ruthenium from organoruthenium compounds.[160] Attempts to extract ruthenium from chloride solutions by 2-thiobenzothiazole,[161] 2-thiobenzimidazole,[162] pyrimidinethiol,[163,164] and di(2-ethylhexyl)phosphoric acid (HDEHP)[165] have been reported.

Solid-phase extraction of ruthenium with 9,10-phenanthrenequinone monoxime into molten naphthalene,[166] 3-hydroxy-2-methyl-1,4-naphthaquinone 4-oxime into microcrystalline *p*-dichlorobenzene,[167] and by polyurethane foam[168] has been investigated. Simultaneous extraction of Ru and Rh was carried out in the system employing 9,10-phenanthrenequinone monoxime.

4. Sorption

Sorption methods are particularly suitable for separation and preconcentration of ultra trace amounts of noble metals from the solutions containing large excess of non-noble metals, *e.g.,* Cu, Fe, Ni, Co, Al, Mg, and Ca. In some systems, the quantitative separation from 10^4-fold quantities of accompanying metals and ~10^3 concentration factors can be achieved.[169–171] The developed methods are convenient for group concentration of precious metals from the samples of rocks, ores, minerals, alloys, and industrial products. Inorganic and organic complex forming sorbents are most often applied in separation procedures.

Sulfides (CuS, HgS, NiS, PbS, SnS_2) and hydroxides (Be, Zn, Fe, La, Ti) have been used for preconcentration of traces of noble metals from the solutions of complex matrices.[170] Low solubility of noble metal sulphides in acidic media makes them particularly attractive for sorption on sulphide collectors. Co-precipitation of ruthenium (Pt, Pd, Rh, and Ir) with a mixed collector, copper sulfide-2-thiobenzothiazol, was employed in analysis of products of processing nickel and copper slimes.[172] Trace amounts of ruthenium were quantitatively sorbed on iron(III) hydroxide at pH > 4.7.[173] The application of different hydroxides to preconcentration of ruthenium (and some non-noble metals) from sea water was reported.[174]

Resins chemically modified with sulphur and nitrogen-containing organic ligands have found the widest application as noble metal sorbents.[169,171,175] Subsequent desorption of the analytes by the use of suitable eluents makes a basis of their mutual separation prior to the detection. The metals can also be determined directly in sorbent phase by detection methods applicable to solid phase.

Polystyrene-divinylbenzene (8%) resin with thiosemicarbazide as functional group effectively sorbed Ru from 1.5 *M* HCl (Pd and Pt from 1 *M* HCl, Rh from 2 *M* HCl).[176] Iridium passes through the column. Ruthenium can be eluted together with rhodium by using 9 *M* HCl. The reduction of ruthenium to Ru(II) (hydroxylamine hydrochloride) which is not sorbed by the resin allows to separate both metals. Sorbents containing *N*,*N*-dialkyl-*N′*-benzoylthiourea bound as an active group to the matrix of a macroporous styrene-divinylbenzene copolymer exhibit significant affinity for precious metals.[177] Ruthenium is characterized by a middle (Pd > Pt > Ru > Rh > Ir) tendency for sorption. The application of polyacrylacylisothiourea chelating fibre for enrichment and separation of trace amounts of Ru, Pd, and Au from the samples containing the excess of Ca and Mg (400-fold excess); Ni, Zn, Cu(II), Al, Fe(III) (200-fold excess), and Co(II) (100-fold excess) was described.[153] Lower (by a factor 2) concentration of interferents could be tolerated when determining ruthenium. Sorption of ruthenium from HCl solutions by silica modified with *N*-allyl-*N′*-propylthiourea and *N*-phenyl-*N′*-propylthiourea has been studied.[178] The content of sorbed ruthenium is largely influenced by the pH of the medium, the presence of reductive agent (tin(II) chloride examined) and other factors. The polymeric thioether $(\text{-CH}_2\text{-S-})_n$ has been investigated as a sorbent for PGM.[179,180] Surface sorbed MCl_xL_y (where L is a polymer thioether link) complexes were identified at the initial sorption stage. They pass into polymeric thiosulphides under heating. Ruthenium undergoes sorption under heating the solution.

Polymeric sorbents with aliphatic and heterocyclic amino groups exhibit high affinity for PGM and ability to their separation from the samples containing large quantities of common metals. The sorption is based on the interaction of anionic complexes of noble metals with protonated amines. The application of chelate forming POLYORGS sorbents, containing nitrogen heterocycle (heterocyclic amine and amidoxime groups) highly selective for all noble metals was discussed.[171]

Ruthenium (Rh and Os) belongs to the group of lower than the other PGM tendency to form complexes with aliphatic amines.[181] Sorption of chloride complexes of ruthenium on an amine polymer with diethylenetriamine functional groups has been investigated.[182] The effective sorption of Ru(IV) from 1 *M* HCl and Ru(III) from the solutions of pH 4 to 5 was reported. Quantitative extraction of ruthenium and the other noble metals from 1 to 3 *M* HCl in the presence of a 10^6 to 10^7 excess of matrix elements (up to 50 g l^{-1} Fe(III) and Cu(II), Ni at 40 g l^{-1}) was achieved on a polystyrene based sorbent with diethylenetriamine groups.[183] The sorption of ruthenium was shown to be affected by a high content (> 0.15 *M*) of sulfate. The sorption of Ru (Pd, Rh and Pt) from 1 to 3 *M* HCl on the polymeric sorbent containing tertiary amino-nitrogen allows their separation from any amounts of Ni and Co, ≤ 40 mg ml^{-1} Cu and 80 mg ml^{-1} Fe.[184] Mixed sorption mechanism by silica bonded aliphatic mono- and polyamines (complexation at pH > 1 and by anion-exchange at pH < 1) has been described for particular noble metals.[181] Separation of all noble metal ions on silica gel with chemically bonded aminopropyl- and thio-substituted ligands has been investigated.[185]

Ruthenium (down to 0.1 ppm) could be determined in the presence of five fold amounts of Cu or Fe(III), 10-fold amounts of Pd, 50-fold amounts of Co, Rh and Pt and 100-fold amounts of Os, Ir and Ni after sorption of its 1,10-phenanthroline complex on the surface of silica sorbents.[186] Synthesis of poly(*N*-aminoethyl)acrylamide chelating fibre and properties of concentration and separation of noble metals, including ruthenium, have been described.[187] Detection limits of 16 ng ml^{-1} for all metals were reported.

5. Chromatographic Methods

Chromatographic methods are well established for the separation of noble metals from associated base metals as well as for mutual separation of particular analytes.[133,188,189] The developed methods for ruthenium generally concern its isolation from multicomponent noble metal mixtures. The separation of ruthenium from some common metals is also possible. Chromatographic methods have been widely employed to study the nature of complex ruthenium species, in particular in mineral acid media.[73]

Ion-exchange chromatography provides major contribution in the field of noble metals separation, in particular from mixtures with base metals. The technique is widely applied for matrix elimination and preconcentration of precious metals. Both cation and anion exchangers can be used in separation procedures. Anionic complexes of noble metals occurring in diluted HCl pass through cation-exchange columns while base metals which exist as cations are retained on the resins. Basic anion exchangers retain anionic complexes of precious metals and none of cations of common metals. Large chemical similarities of PGM and strong affinity to the resins provide difficulties with their subsequent separation and even with complete elution of particular analytes from anionic exchangers. In some systems, differences in the strength of electrostatic interaction of the examined complexes with the resins or lability to form species of different activity allow separation of some multicomponent mixtures.

The majority of chromatographic methods have been developed for chloride complexes of PGM being the products of most digestion procedures. A quantitative conversion of particular analytes into a definite complex is required prior to the separation step due to differences in the chromatographic behaviour of various species. The conversion of the noble metals into doubly charged complexes, MCl_6^{2-}, prior to the separation employing anion-exchange resins is advantageous. Doubly charged chloride complexes are strongly sorbed by the resins, whereas triply charged complexes, MCl_6^{3-}, are weakly bound. Complex nature of ruthenium species in aqueous solution, a labile character of complexes toward aquation and the ability to change the oxidation state contribute to difficulties in developing reliable chromatographic procedures for its separation. The age of the solution is an important factor due to changes in the composition of the examined complex that may occur in time.

Retention of ruthenium from chloride solutions obtained from the samples pretreated with HF-HNO_3-HCl by Dowex 1-X8 anion exchange resin was studied.[190] A high affinity of the exchanger for noble metals in diluted HCl significantly lowers with increase in HCl concentration. Perchloric acid decreases the recovery of ruthenium while present in the examined solutions. It could be removed prior to the chromatografic separation by evaporation with HCl. Thiourea solution was examined as an eluent for ruthenium as well as for platinum, palladium and gold from the resin. The 92% recoveries of Ru (500 μg Ru, 75 ml 0.3 *M* thiourea in 0.1 *M* HCl) and > 97% of Pt, Pd, and Au were achieved. Rhodium was partially eluted under the conditions used; iridium remained bound to the resin. Concentrated hydrochloric acid can be used for complete elution of all analytes. The application of the resin not being in contact with thiourea prior to the separation step is advantageous.

Ruthenium (Pd, Ir, and Pt) can effectively be retained from 1 *M* HCl on the anion-exchange Bio-Rad AG 1-X8 resin.[191] Lower retention of the analytes at higher acid concentrations was also reported. A mixture of 5 *M* HCl and 5 *M* $HClO_4$ was applied for simultaneous elution of the metals. Various oxidizing agents (H_5IO_6, $KMnO_4$, $K_2Cr_2O_7$, and Cl_2) were examined to convert the analytes into oxidation states of higher affinity to the resin. The application of Bio-Rad AG 1 × 8 resin for isolation of Ru (Pd, Ir and Pt) and the siderophile elements (Re, Ag, Zn and Cd) from silicate rocks was described.[192] Successive elution of particular analytes with 0.8 *M* HNO_3 + 10% Br_2 (Zn, Cd), 11 *M* HCl (Ag, Ru), 8 *M* HNO_3 (Pd, Re) and 13.5 *M* HNO_3 (Ir, Pt) was carried out. The 70 to 75% procedural yields for ruthenium was reported. The elution of ruthenium by 8 M HNO_3 at approx. 90^0C was also investigated. The use of fresh Dowex 1-X8 resin has been recommended for chromatographic separation of Ru (Pt, Pd, and Ir) from environmental samples to avoid strong memory effects.[193]

Strong basic anion exchanger, Amberlite IR 400, was applied to separate and preconcentrate ruthenium and the other noble metals from silicate rock samples digested in HF and *aqua regia*, fuming the solution with sulphuric acid and dissolving the residue in 2 M HCl.[194] Ruthenium was quantitatively eluted from the resin by using 0.25 *M* HNO_3. Two steps elution by using 0.25 *M* HNO_3 and 1 *M* NH_4OH as eluents was applied for palladium, platinum and rhodium. Elution of osmium, iridium, and gold was incomplete while using both eluents.

The application of anion-exchange paper, Reeve Angel SB, allows the separation of microgram quantities of ruthenium from osmium and from large proportions of Cu, Fe and Ni.[195] The 91.5% retention of ruthenium from slightly acidic solution (pH 3) was achieved.

Procedures for quantitative separation of ruthenium and the other noble metals from base metals using cation-exchange resin, Amberlite CG-120, was described.[196] Elution with 0.2 *M* HCl yielded the analyte recoveries > 99%. Cation-exchange chromatography (a Dowex 50W-X8 resin) allowed the separation down to 5 μg Ru from 500 mg of Cu (matrix Cu eluted with 3 *M* HCl) and larger amounts (100 μg Ru) from 200 to 500 mg of Al, Ca, Fe, Mg, Mn, Ni, and Zn.[197] Complete recovery of ruthenium (from μg levels) and the other PGM (except Os), Au, and Ag was obtained using a Dowex 50W-X8 resin for separation of the analytes from matrix elements in geological materials (ores, concentrates, mattes and silicate and iron formation rocks) followed the decomposition of the samples in HF and *aqua regia* and fusion of the insoluble residue with sodium peroxide.[76,78]

The conversion of noble metals into complexes with suitable organic reagents enables the use of the other chromatographic techniques for their separation. High-performance liquid chromatography (HPLC) is capable of separating of multicomponent noble metal mixtures as well as their mixtures with some non-noble metals. The complexes with 8-hydroxyquinoline and its derivatives,[198–201] diethyldithiocarbamate,[202] thiourea derivatives,[150] 1,10-phenanthroline,[203,204] substituted 5-diethylaminophenol,[205–209] 4-(5-nitro-2-pyridylazo)-resorcinol,[210,211] 4-2(thiazolylazo)resorcinol,[212,213] 4-(2′-thiazolylazo)resacetophenone oxime[214] and 1-(2-pyridylazo)-2-naphthol-6-sulfonic acid [215] were used in chromatographic procedures for separation and preconcentration of various noble metal mixtures containing ruthenium.

Stable neutral chelates of all platinum metals with 8-hydroxyquinoline were effectively separated by normal phase HPLC on a column packed with Silasorb 600 silica gel by elution with methylene chloride-propan-2-ol mixture (97:3).[200] The chelates were eluted in the order of retention times Pt < Pd < Os < Ru < Ir < Rh. Earlier[198] the Silasorb 600-chloroform-propan-2-ol (98:2) system was applied to separate 8-hydroxyquinolinates of Ru, Pt and Pd. The separation of the Ru, Pt, Mo and Co complexes was also possible under the conditions applied. The binary mixtures of Ru and Pd could be separated by ion-pair reversed phase HPLC on a Separon C_{18} column with acetonitrile-acetate buffer (pH 6)-H_2O (7:2:1) containing hexadecyltrimethylammonium bromide after preliminary conversion of the analytes into the complexes with 7-phenylazo-8-hydroxyquinoline-5-sulfonic acid.[201]

Attempts to isolate Ru-1,10-phenanthroline complex from the mixture with analogeous complexes of Fe and Ni on the polystyrene-divinylbenzene polymer based columns and acetonitrile-water-perchloric acid mixture as mobile phase were reported.[204] Conversion of ruthenium into the complex with 2-(6-methyl-2-benzothiazolylazo)-5-diethylaminophenol allows its separation from the other noble metals: Pd, Ir, and Pt,[206] Os, Ir, and Pt[207] and Rh, Os, Ir, and Pt[208] as well as from the mixtures with some transition metals: Co and Ni[206,207] and Co, Ni, and Cu.[208] Retention of ruthenium chelate with 1-(2-thiazolylazo)-5-diethylaminophenol on C_{18} column was examined.[205,209] The developed separation methods were suitable for isolation of ruthenium from the mixtures with Pd, Rh, Ni, and Cu[205] and Pt, Ir, Rh, and Os.[209]

Ruthenium was quantitatively separated from Pd, Rh and Pt[210] and from Nb, V, Co, Fe, Ni and Pb[211] after conversion into the complex with 4-(5-nitro-2-pyridylazo)resorcinol. Methanol-water containing acetate buffer (pH 5.0) and tetrabutylammonium bromide was considered as optimum mobile phase. The use of 4-(2-thiazolylazo)resorcinol as a precolumn derivatization agent allowed the separation of Ru, Rh, Os, Co, and Cu[212] and Ru, Os, and Rh.[213] The metal chelates were separated on C_{18} stationary phase with acetonitrile-acetate buffer (3:7) (pH 5) or methanol-water (3:2) mixture (pH 4.0) as mobile phases. Tetrabutylammonium bromide was used as an ion-pairing reagent. The separation of ruthenium from Rh, Co and Cu was also possible on a Nucleosil C_{18} column using 1-(2-pyridylazo)-2-naphthol-6-sulfonic acid as a precolumn derivatization agent.[215]

Reversed phase HPLC has been applied to control the synthesis of $[(bpy)_2RuL_2]^{2+}$ (where bpy is 2,2′-bipyridine) class of compounds.[216] The isolation of the complex $[(bpy)_2RuIm(H_2O)]^{2+}$ (where Im is imidazole) was possible.

Quantitative separation and enrichment of Ru, Pd, Rh and Au from sample solutions of pH 5 to 9 on a macroporous poly(vinylaminoacetone) chelating resins was achieved.[217] A mixture of 4 *M* HCl and 3% thiourea solution was applied for desorption of ruthenium. Traces of Ru (Au, V, and Ti) were separated and pre-concentrated on poly(epoxymelamine) chelating resin.[218] The absorbed analytes were eluted with 1 *M* HCl containing 2% thiourea.

Diastereoisomeric resolution of *bis*-(2,2′-bipyridyl)ruthenium(II) complexes containing alanine, phenylalanine and tyrosine ligands has been reported.[219] The chromatographic behavior of trinuclear ruthenium acetylido-carbonyl compounds[220] and amino-acidatoruthenium(II) complexes[221] has been examined. Chromatographic interactions of $Ru(bpy)_3{}^{2+}$ complex with silica-based stationary phases were studied.[222]

The application of thin-layer chromatography (TLC) for separation of the noble metal multicomponent mixtures was decribed.[63,223–228] The methods are based on differences in the extractability of the metal chelates formed under the action of chromatographic chelating agents. The use of cellulose ion-exchangers in separation procedures was also reported.[223] Ruthenium from mixtures with Pt, Os and Co could be effectively separated on a Silicagel 60 stationary phase after conversion into chelates with *N,N*-dialkyl-*N′*-benzoylthiourea and using pure solvents of medium polarity like $CHCl_3$, benzene, toluene or xylene as mobile phase.[224] All six platinum metal 8-hydroxyquinolinates were well separated by HP TLC (a Silicagel 60, tetrahydrofuran-$CHCl_3$ (1:9).[228] Phenylhydrazine-*N*-carbodi-thioates of ruthenium, rhodium and palladium were separated from each other and from the complexes of the other group VIII metals (except Co) on Silicagel G with $CHCl_3$, benzene, acetonitrile-CCl_4 (1:4) or ethyl acetate-CCl_4 (1:4).[225] The thin-layer chromatographic behavior of various tris(β-diketonato) complexes of Ru (Co and Cr) on silica gel with different non-aqueous mobile phases was examined.[227] It was found that the R_f values of the complexes were increased by the substitution of an *O*-containing ligand with a ligand containing less electronegative S.

Successful separation of all noble metals (except Os) on ECTEOLA-cellulose in HCl medium with or without hydrogen peroxide was achieved.[223] 3 to 5 *M* HCl was considered as the best medium to avoid hydrolysis of the analytes. The addition of H_2O_2 was recommended to preserve quadrivalent state of Ir yielding a single spot of the metal. R_f values of the metals decreased in the order $Ir \geq Rh > Ru > Pd > Pt > Ir (IV) > Au$.

Size-exclusion HPLC was used for monitoring interactions of ruthenium based antitumor drugs: imidazolium *trans*-tetrachloro-*bis*(imidazole)ruthenate(III) (HIm-*trans*[$RuCl_4im_2$]), sodium *trans*-tetrachloro-*bis*(indazole)ruthenate(III) (Na-*trans*[$RuCl_4ind_2$]) and indazolium *trans*-tetrachloro-*bis*(indazole)ruthenate(III) (HIn-*trans*($RuCl_4ind_2$]) with human serum proteins (albumin and transferrin) to evaluate of the complexed and free drug fractions.[229] Polymer gels (Superdex^{TM}-75 HR 10/30 SEC (spherical composite of cross-linked agarose and dextran) and a Progel TSK-GEL PW_{XL} (spherical porous cross-linked polydivinyl benzene)) were preferred to silica gels to avoid the interactions between the column stationary phase and the analytes. Short (4 cm) columns allowed the analyte response to be obtained within a few minutes.

Separation of ruthenium and the other noble metal chloro complexes by capillary electrophoresis (at –10 kV with an electrolyte of HCl/NaCl at pH 2.4) was illustrated.[230]

III. DETERMINATION METHODS

A. Gravimetric and Titrimetric Methods

Difficulties with quantitative precipitation of ruthenium in the form of compounds of definite compositions limit the number of gravimetric methods developed for its determination. Ruthenium can be precipitated as hydrated Ru(IV) oxide ($RuO_2{\cdot}H_2O$), sparingly soluble sulfides and complexes with some organic reagents, *e.g.,* thionalide, thioacetamide, thiourea, and benzidine.[42,126,231] Metallic ruthenium obtained under reduction of the obtained compounds in hydrogen is the recommended weighing form.

Hydrated ruthenium oxide precipitates in the presence of ammonium carbonate from chloride, nitrate and perchlorate media after removal of the excess of acids. Platinum(IV) is the only PGM that does not interfere with hydrolytic precipitation of ruthenium. The other metals also form sparingly soluble hydrolytic products.

Gravimetric determination of Ru(VIII,VI) as Ru(IV) oxide obtained by reduction with $NaBH_4$ at pH 9 to 12 was described.[232] $RuO_2{\cdot}2H_2O$ identified as a reduction product was used as a weighed form after dewatering at 400 to 450^0C.

Quantitative precipitation of ruthenium (within the range of 1.05 to 8.34 mg Ru) in the form of mixed $TlRu_2S_6$ sulfide was reported.[233] The precipitation was performed under the treatment with hydrogen sulfide in the presence of thallium.

Gravimetric method for the determination of ruthenium (0.05 to 0.2 g Ru) and the other noble metals (in alkaline, slighty acidic or neutral solutions) by means of the reduction of the analytes to elemental form with noramidopyrine has been proposed.[234]

Classical titrimetric methods developed for the determination of milligram amounts of ruthenium are based on the redox reaction Ru(VIII) ↔ Ru(IV) and Ru(IV) ↔ Ru(III).[42] Tin(II) chloride, KI, $TiCl_3$, VSO_4, and $C_6H_4(OH)_2$ were applied as reductant agents. The conversion of ruthenium into Ru(VIII) under the action of Ce(IV) or $Pb(CH_3COO)_2$ was also used in titrimetric procedures.

Titrimetric methods are often combined with spectrophotometry and electrochemical techniques. The use of electrogenerated titrants, *e.g.,* $CuCl_n^{(n-1)-}$,[56] Fe(II),[235] and quinol[236] has been described. The method allowing simultaneous titration of Os(VIII) and Ru(VI) using two titrants, sodium tetrahydroborate and hydroxylamine, and potentiometric detection has been developed.[237]

Ruthenium has been determined by titration with ethylenediaminetetraacetic acid (EDTA) (pH 2-3).[238] Amplification method for the determination of trace amounts of ruthenium based on the oxidation of Ru(II or III) with sodium periodate (pH 2.4 to 3.6) followed by titration of the released iodine with sodium thiosulfate has been proposed.[239]

B. Spectrophotometry UV-VIS

Spectrophotometry UV-VIS is widely applied to the determination of microgram amounts of ruthenium. Transformation of ruthenium into stable soluble species that can make the basis of spectrophotometric measurement provides main difficulties in developing reliable spectrophotometric methods. Great chemical similarity of noble metals resulting in formation of complexes of similar compositions and properties causes the necessity of separation of ruthenium from the other noble metals, in particular from osmium, prior to the detection. The developed spectrophotometric methods are generally combined with separation and preconcentration steps. Distillation, solvent extraction and flotation procedures have found the widest applications for combination with spectrophotometry. Complexes of ruthenium with inorganic ligands, such as chlorides, thiocyanates and $SnCl_3^-$ groups, and various organic reagents make the basis of spectrophotometric methods developed.[240–242]

Larger amounts of ruthenium can be determined directly in aqueous solutions of RuO_4 (ε= 2.7·10^3 l mol^{-1}cm^{-1} at 309 nm),[243] RuO_4^{2-} (ε=1.7·10^3 l mol^{-1}cm^{-1} at 465 nm)[84,244,245] or RuO_4^-.[246] The tetroxide method allows the determination of ruthenium (up to 32 μg ml^{-1}) in the presence of osmium while using the second-order derivative spectrophotometry. The method has been applied to the determination of ruthenium in the plasma standard solution. The ruthenate was used to determine ruthenium in the compounds utilized in electronics: ruthenium dioxide, lead ruthenite and bismuth pyroruthenate.[84] Ruthenium (24.4 to 24.9%) in organoruthenium compounds has been determined by extraction of perruthenate with benzyltributylammonium chloride into $CHCl_3$.[160]

Ruthenium, within the range of 0.07 to 20 μg ml^{-1}, can be determined in the form of chloride complex, $RuCl_6^{2-}$, directly in solutions obtained after absorbing the volatile RuO_4 in 6 to 8 *M* HCl.[45,47,55] The molar absorptivity (ε) of the $RuCl_6^{2-}$ complex amounts to 4.8·10^3 l mol^{-1}cm^{-1} at λ_{max} = 480 nm. Osmium up to 100 μg ml^{-1} does not interfere with the determination of ruthenium. The application of differential spectrophotometry to the determination of ruthenium in bismuth (lead) ruthenites doped with neodymium using chloride complexes of the metals in 6.5 *M* HCl has been described.[247]

A violet-blue thiocyanate complex of ruthenium formed in 0.8 to 1.2 *M* HCl and 0.25 to 0.35 *M* SCN$^-$ after 3 to 5 min heating the solution makes the basis of extraction(MIBK)-spectrophotometric methods (ε = 5.5·10^3 l mol^{-1}cm^{-1} at $_{max}$ = 570 nm).[138,248] Extraction of ruthenium thiocyanate complex into the surfactant phase with Zephiramine and Triton X-100 makes the basis of more sensitive method (ε = 1.16·10^4 l mol^{-1}cm^{-1} at 565 nm).[142] The first derivative spectrophotometry was used to reduce the interferences from the other PGM.

Ruthenium, similarly to the other platinum metals, reacts with $SnCl_3^-$ ligands (tin(II) chloride in hydrochloric acid) by forming a yellow-orange (amber) anionic complex, $RuCl_2(SnCl_3)_2^{2-}$, that can make the basis of spectrophotometric determination of the metal (ε = 2.7·10^3 l mol^{-1}cm^{-1} at 445 nm).[249–252] Easy transformation of ruthenium from various forms occurring in chloride solutions into the $RuCl_2(SnCl_3)_2^{2-}$ complex is the advantage of the method.

A derivative spectrophotometric method allowing selective determination of ruthenium (within the range of 2 to 35 μg ml^{-1}) in the presence of osmium (up to 450 μg ml^{-1}) by the use of anionic complexes of both metals with tin(II) chloride has been developed.[253] The method has been applied to the determination of ruthenium in waste solutions. Ruthenium in carbon supported Pt-Ru(3) catalyst was determined directly in solutions obtained after digestion of the examined samples by the use of the complex with tin(II) chloride and numerical calculation of the second-order derivative values of the absorption spectra of mixtures with platinum.[254]

The $RuCl_2(SnCl_3)_2^{2-}$ complex can be extracted from aqueous solutions in the form of ion-pairs with high-molecular-weight amines.[114,146] The methods for simultaneous extraction of Ru and Pt with trioctylamine and diantipyrylmethane (in 1,2-dichloroethane) and the determination of the metals in the presence of each other in organic solutions obtained by employing derivative spectrophotometry have been recently published.[146]

The anionic complex of ruthenium with tin(II) chloride associated with basic dyes, Rhodamine 6G[250] or Crystal Violet[251] makes the basis of very sensitive flotation-spectrophotometric methods (ε = 5.0·10^5 l mol^{-1}cm^{-1} and 2.1·10^5 l mol^{-1}cm^{-1}, respectively). The Rhodamine 6G method was applied to the determination of traces of ruthenium in technical-grade platinum.

Numerous spectrophotometric methods using various organic chromogenic reagents have been developed for the determination of ruthenium. Reagents containing sulfur and nitrogen as donor atoms have found the widest applications for the determination of small amounts of ruthenium in various materials.

Thiourea reacts with ruthenium in HCl medium to form a blue $Ru(NH_2CSNH_2)_6^{3+}$ complex[255] widely used for the determination of the metal. Recent experiments have shown that quantitative transformation of ruthenium into the thiourea complex ($\varepsilon = 2.9 \cdot 10^3$ l mol^{-1} cm^{-1} at 640 nm) takes place in 5 *M* HCl and 1% thiourea solution after 15 min heating at 70^{0}C.[256] The rate of reaction strongly depends on the form of ruthenium in the examined solution. Ruthenium tetroxide slowly reacts with thiourea. The reaction is faster when ruthenium occurs in the form of chloride complexes. Platinum, palladium and rhodium at the mass ratio of 15:1 (Pt) and 18:1 (Pd and Rh) do not interfere with the determination of ruthenium. Osmium affects the results for ruthenium at the mass ratio ≥ 1.5. The complex of ruthenium with thiourea has been used to determine ruthenium in carbon supported Pt-Ru(0.5)-Ge catalysts,[256] nitroso[257] and carbonyl[258] complexes. The irradiation with ultraviolet light was applied to labilize nitroso and carbonyl complexes prior to the chromogenic reaction.

Ruthenium can be determined in the presence of tenfold amount of osmium after transformation into the complex with 1,4-diphenylthiosemicarbazide extractable into $CHCl_3$ ($\varepsilon = 1.01 \cdot 10^4$ l mol^{-1}cm^{-1} at 560 nm).[259] The reagent has been used to determine Ru in meteorites,[260] Pt-Ru(4)[74] and Pt-Ru(20) alloys.[261]

Dithizone reacts with Ru(VIII and VI) at 20^{0}C and with inert Ru(IV) complexes at 85^{0}C to form a primary 1:3 dithizonate that can be concentrated (*ca*. 20-fold) by extraction into $CHCl_3$.[262] The determination of ruthenium traces (5 ppb) by this procedure has been reported. Extraction($CHCl_3$)-spectrophotometric method ($c_{Ru} = 0.05$ to 6.5 μg ml^{-1}) based on the complex of ruthenium with *o*-thioacetoacetanilide in the presence of γ-picoline (acting as a synergic agent) has been described.[263] Extraction has been carried out in the presence of appreciable quantities of various foreign ions, including platinum metals. The complex with octadecyl- dithiocarbamate has been used to determine ruthenium (within the range of 0.5 to 6 μg ml^{-1}) in the presence of rhodium by derivative spectrophotometry.[264] Ruthenium in binary mixtures with Co(II), Cu(II), Fe(III) and Ni(II) containing a 50-fold excess of the base metal has been determined with pyrimidine-2-thiol after preliminary extraction with *N*-octylaniline.[265]

1,10-Phenanthroline was applied to determine ruthenium in organometallic compounds.[266,267] The use of microwave radiation allows significant decrease (more than 20 times) of the time of complex formation.[268] Studies on the determination of ruthenium (within the range of 9.6 to 450 ng ml^{-1}) in the presence of iron by the use of binary complexes of the metals with 4,7-diphenyl-1,10-phenathroline (bathophenanthroline) in the presence of ethyleneglycol by derivative spectrophotometry have been reported.[269] Spectrophotometric studies on the application of 8-hydroxyquinoline ($CHCl_3$, $\varepsilon = 1.2 \cdot 10^4$ l mol^{-1}cm^{-1} at 420 nm)[156] and the ferroin yielding *as*-triazines [270] to the determination of ruthenium have been reported.

The applications of thiohydrazides[271] and thiosemicarbazone[272] to the determination of noble metals, including Ru, have been published. Examinations of azorhodanines,[273–275] azobenzeneazorhodanine derivatives in the presence of surfactants[276] and some azoxines[277] as spectrophotometric reagents for noble metals, including ruthenium, have been described.

Spectrophotometric methods based on ion-associates of anionic complexes of ruthenium (chlorides, complexes with $SnCl_3^-$ ligands, thiocyanates) with basic dyes (Rhodamine 6G,[47,48] Crystal Violet, Victoria Blue B[251] and Capri Blue[278]) undergoing flotation preconcentration while shaking an aqueous solution with a non-polar organic solvents (*e.g., n*-hexane, cyclohexane, toluene, or xylene) provide the highest sensitivity (ε within the range of (2 to 5)10^5 l $mol^{-1}cm^{-1}$) of the determination. The solutions obtained after dissolving the ion-associates in organic polar solvents (*e.g.,* methanol, acetone) make the basis of spectrophotometric measurements. Low selectivity is the disadvantage of flotation-spectrophotometric methods. The separation of ruthenium from the other elements, in particular from osmium, is required prior to the detection. Detailed discussion of the solvent flotation methods combined with spectrophotometry has been published.[130]

Attempts to determine ruthenium by spectrophotometry combined with solid-phase extraction with 3-hydroxy-2-methyl-1,4-naphthaquinone into microcrystalline *p*-dichlorobenzene[167] or loaded into polyurethane foam[168] have been described. A chemiluminescence method based on the catalytic effect of Ru(III) on the oxidation of proflavine-*N,N,N′N′*-tetraacetic acid by H_2O_2 was reported to offer a DL of 1 ng ml^{-1}.[279]

Chemical amplification methods based on the oxidation of Ru(II or III) with periodate (pH 2.4 to 3.6) and determination of the released iodine by spectrophotometry as triiodide (at 350 nm) have been described.[239]

C. Atomic Absorption Spectrometry

Atomic absorption spectrometry has widely been used for the determination of precious metals in a large variety of samples such as ores, rocks, industrial products, waste solutions and solids (including nuclear wastes), clinical, biological, and environmental materials. The detection limits offered by the technique depend on the atomizer used and the kind of the matrix. It is generally in the order of μg ml^{-1} and sub-ng ml^{-1} (pg as a characteristic mass) for flame and graphite furnace atomizer, respectively. Much consideration is required to quantitative digestion of the examined samples and preconcentration of the metals in analysis of materials of lower concentration of the analytes than the DL offered. The 349.9 nm line is the most sensitive for ruthenium.

The effects of flame type, buffers, acids, and matrix elements on the flame atomic absorption spectrometric (FAAS) signal of ruthenium have been investigated.[280–285] The application of air-acetylene and nitrous oxide-acetylene flames to the determination of ruthenium in Purex waste solutions was examined.[282] Lower sensitivity (by a factor of 2.5) and the poorer signal to noise ratio were obtained with N_2O–acetylene flame. Detection limits of 0.1 μg ml^{-1} Ru and 0.35 μg ml^{-1} Ru for the triple beam-passage in the air-acetylene and nitrous oxide–acetylene flame, respectively were reported. Cerium(III) was the only element that exhibited a decreasing effect on the signal of ruthenium using air-acetylene flame. The magnitude of cerium interference depended on the flame stoichiometry, the number of beam passage and the Ce : Ru ratio. The addition of cerium to a calibration solution has been recommended. Identical signals were recorded from ruthenium nitrosyl, ruthenium chloride, and ruthenate compounds. The addition of Ce(IV) to the sample solution containing 0.25 to 125 μg Ru in 0.5 to 1 *M* HNO_3 resulted in the 60-fold enhancement of sensitivity for ruthenium in FAAS[283] owing to improved transport and atomization efficiency of RuO_4 formed.

Phosphorous acid causes strong interferences in the determination of ruthenium by FAAS.[284] The 25% and 65% decrease in the Ru signal in the presence of 0.1% and 2% phosphorous acid in the examined solutions, respectively, was reported. The interference was alleviated by buffering the solutions with $La_2(SO_4)_3$ or $KHSO_4$. Better precision was reached with lanthanum buffer. Iron and rhodium interfere with ruthenium signal in both air-acetylene and N_2O-acetylene flames. Iron at concentrations of 10, 100 and 1000 µg ml^{-1} depresses the signal of Ru by about 10, 70 and 90%, respectively. Rhodium at 10 and 100 µg ml^{-1} increases the results for ruthenium by about 10 and 20%, respectively.

Mutual effects of Ru, Pt and Rh using N_2O-acetylene flame and the interference from some cations (Al^{3+}, K^+, La^+, Mg^{2+}, and Na^+) as well as associated anions (Cl^- and SO_4^{2-}) on the AAS measurements were investigated.[281] $La_2(SO_4)_3$ was used as a spectroscopic buffer. DL of 1.25 µg ml^{-1} was reached for ruthenium. Poor sensitivity of the determination of ruthenium (and Os) was reported when employing copper and sodium ions as buffers.[280] The use of Ce buffer was recommended to alleviate the interference from Fe and Si in analysis of some Ru catalysts.[285]

A significant influence of the chemical form of ruthenium in the examined solution on its AAS signal in air-acetylene flame has been observed.[286] Chlorides, nitroso chloro and nitroso nitrato complexes of ruthenium give higher signals than nitro-, nitroso nitro-, ammino and sulfate complexes. Different effects of mineral acids as well as some cations (Na^+, K^+, NH_4^+, Rb^+, and Cs^+) were observed while ruthenium existed in various forms in the examined solutions. Hydrochloric acid decreased the signals of chloro and nitroso chlorocomplexes, while the signals of nitroso nitro complexes were increased. The effects of $CuSO_4$ buffer on the sensitivity of the determination of ruthenium (for $Na_2RuNO(NO_2)_4OH$ in the examined solution) in the presence of Rh and Ir were studied.

The substantial increase of the signal of ruthenium was obtained in the presence of CN^- ions.[287] No interference from many cations (K^+, Na^+, Cs^+, Ca^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Mg^{2+}, Ba^{2+}, Cu^{2+}, Al^{3+}, Fe^{3+}, Rh^{3+}, NH_4^+, UO_2^{2+}) and anions (NO_3^-, $PdCl_4^-$ and $PtCl_4^{2-}$) was observed. EDTA, maleic and oxalic acid at 200 µg ml^{-1} concentrations did not interfere with the determination of ruthenium. The high stability of ruthenium cyano complexes is responsible for the elimination of interferences.

The determination of ruthenium in organic solutions containing toluene and 1-hexene, 1-heptanal or 1-heptanol was investigated.[288] The DL of 0.62 µg ml^{-1} Ru was reported. Ethanol and MIBK were applied as diluents of the examined solutions. The use of ethanol was found advantageous.

Detection limits offered by FAAS are not sufficient for the determination of ruthenium in many materials. Much effort has been done to the development of electrothermal atomic absorption (ETAAS) methods, often combined with preconcentration steps. The proposed ETAAS methods usually deal with the determination of ruthenium in mixtures with the other noble metals. The evaluation of the effects of the other noble metals on the Ru signal has been a subject of extensive research. Attempts to determine ruthenium in rocks, ores and metallurgical samples,[76,78,158] industrial products,[289] copper[290] and lead[291] alloys, biological materials,[292] water samples,[131] dendrimers,[293] high purity platinum,[294] and radioactive waste[295] have been described.

The mechanism of atom formation and vaporization of ruthenium (and the other noble metals) from the wall of graphite-tube atomizer was discussed.[296,297] The conversion of the elements to the metallic state prior to vaporization as atomic vapours was stated. Identical mechanism of atomization of all metals was concluded. The temperatures of 950 K and 2430 K as corresponded to the complete conversion of ruthenium in a carbon furnace atomizer into the elemental state and its sublimation, respectively, were estimated.

The effects of PGM and common metals on ETAAS signal of Ru were investigated.[158,289,298–300] Intermetallic compounds probably formed in gaseous phase were found to be a reason of lower atomization of ruthenium in the presence of Pt, Pd, Fe, Co, Ni, and Cu.[298] No interference from Au, Pd, Pt, Ir and Rh (up to 50-fold excess of each metals) was observed after their group extraction with alkylaniline from the solutions containing Cu, Fe, Co, and Ni (of 2% of total concentration).[299] The evidence of complete elimination of most interference caused by 22 elements examined on the GFAAS signal of ruthenium by using tantalum carbide-coated graphite tube was given.[300]

Simultaneous determination of Ru, Rh, Pt, and Ir in one firing was possible using a pyrolytically-coated graphite furnace in the Hitachi Z-9000 multielement atomic absorption spectrometer equipped with Zeeman background correction.[78] The obtained results were compared with those obtained by using a Varian single-element graphite tube atomizer (Model GTA-95) in combination with a Varian AA-475 spectrometer.[76] The sensitivities for ruthenium of 26 pg and 30 pg using both instruments, respectively, were achieved. The atomization temperatures of 3000^0C and 2700^0C, respectively, were found to be sufficient. Ruthenium and the other noble metals (except Os) were determined in silicate rocks, ores and metallurgical samples after HF-*aqua regia* digestion and separation from matrix elements by ion exchange chromatography and co-precipitation with tellurium. The methods were tested with Canadian certified reference materials.

The effect of Fe and the other noble metals on the determination of Ru after preliminary extraction from copper-nickel ores by a mixture of alkylaniline hydrochloride and petroleum sulphide was investigated.[158] The 5000 to 10,000 ratio of iron to ruthenium in the extracts was found as limiting. The method has been recommended for the determination of ruthenium at the concentration of 0.02 mg kg^{-1} (5-g sample and 5 ml volume of extractant).

Extraction-GFAAS method for the determination of Ru ($4.9 \cdot 10^{-3}$%) and Pt ($8.9 \cdot 10^{-3}$%) and Ir ($7.5 \cdot 10^{-3}$%) in industrial products containing 30% Ni, 30-50% Cu and 3-5% Fe was described.[289] The $MgCl_2(NiCl_2)$-HCl(HBr)-H_2O-diethyl ether three phase extraction system and tin(II) chloride complexes of the noble metals were used to separate the analytes from matrix elements. The determination of PGM (among them Ru) after extraction with di-2-ethylhexyl-dithiophosphoric acid from HCl, H_2SO_4 and H_3PO_4 solutions and their mixtures was investigated.[301] The absorbance of organic extracts ($CHCl_3$) of RuO_4 obtained after oxidizing of the metal in the presence of $NaIO_4$ was measured to evaluate the content of ruthenium (DL 10 ng ml^{-1} Ru) in meteorite samples.[302]

The applicability of ETAAS to the determination of Ru (Pt, Pd, Rh and Ir) in a copper alloy directly in solutions obtained after digestion of the samples with *aqua regia* followed by evaporation with HCl was examined.[290] The matrix ($CuCl_2$) was eliminated in a graphite boat introduced into the electrothermal furnace at 1500^0C for 5 min and at 1300^0C for 0.5 to 5 min dependently on the concentrations of noble metals (0.00015 to 0.001% and 0.003 to 0.03%, respectively).

The ETAAS procedure for the determination of ruthenium in biological samples (tumor, liver, and kidney tissue in the form of aqueous homogenate) has been described.[292] The temperature program: drying at 100^0C (60 s), ashing at 1200^0C (30 s) and atomization at 2600^0C (3 s) was applied. The detection limit of 14.77 to 23.6 ng g^{-1} Ru in tissue was reported.

The effects of various cationic and anionic species on the determination of Ru separated from water samples by co-precipitation with chitosan were investigated.[131] Ruthenium was detected in solutions obtained after dissolving the precipitate in acetic acid.

Slow injection (2.0 μl s^{-1}) of the solution into pyrolytically-coated graphite cuvette using an automatic sampler was applied. A constant and maximum absorbance was observed within the ranges of 700 to 900^0C and 2500 to 2700^0C for ashing and atomization temperatures, respectively. The 100-1000 excess of Ca, Mg, Cu(II), Ni, Fe(III), and Pb(II) as well as 5000 excess of Cl^-, NO_3^-, SO_4^{2-}, and CO_3^{2-} were tolerable. Fair interferences from 100-fold excess of Os(IV), As(III) and Sn(II) observed for synthetic mixtures were negligible in analysis of water samples examined.

The GFAAS method for the determination of ruthenium (DL 65 pg Ru) in dendrimers (supramolecular species of Ru(II) and Os(II) centers connected by polypyridine-like ligands) has been developed.[293] Ruthenium has been detected directly in solutions obtained after dissolving the samples (2.00 to 3.00 mg) in acetonitrile (0.2 to 0.4 ml) and diluting with 1% HCl. The linearity extended up to 4 ng Ru injected. The effects of acetonitrile and HCl up to 10% were negligible. No interference from Os (as $(NH_4)_2OsCl_6$ examined) was observed up to a six-fold excess of Os to Ru. Slight enhancement of the results (*ca.* 5%) was caused by Rh (as *tris*(1,10-phenathroline)chloride) at two-fold excess of Rh to Ru.

Ruthenium (Rh and Ir) was determined in high purity platinum after matrix separation by double extraction from 6 *M* HCl with isoamyl alcohol-MIBK.[294] Poorer extractability of chlorocomplexes of the analytes than Pt(IV) by the solvents used makes the basis of separation procedure. The effect of small amounts of Pt remained in aqueous solution was alleviated by standard addition method. Strong interference from platinum on the AAS signal of Ru was reported earlier.[298] Mutual interferences of Ru and Ir were observed with a > 50-fold excess of either over the other. The method has been recommended to the determination of minimum 2 μg g^{-1} Ru.

Solid sampling methods using a graphite as a diluter and a slurry method based on direct suspension of the sample in a matrix modifier solution were examined for the determination of Ru (Mo, Rh, and Pt) in radioactive simulated waste of the nuclear fuel cycle[295] and a lead alloy.[291]

A review of FAAS and GFAAS methods applied for the determination of noble metals, including ruthenium, in minerals, industrial products, and various metal alloys was presented.[303] The use of Ru as an effective chemical modifier for thermal stabilization of various elements in GFAAS was reported.[304,305]

D. Atomic Emission Spectrometry

Higher selectivity of the determination of noble metals by atomic emission spectrometry makes the technique advantageous to AAS. The AES is however less frequently applied in analysis of ruthenium samples mainly due to poorer DL, in particular as compared with ETAAS. The majority of developed methods concern the determination of ruthenium in mixtures with the other noble metals. The 372.8 nm and 348.9 nm emission lines are the most often used for the detection of ruthenium.

The capabilities of emission flame spectrometric detection of traces of Ru (the other PGM, Au and Ag) using different atomizers were investigated.[306] The application of N_2O-acetylene flame and La as a spectroscopic buffer was recommended to eliminate the interfering effects of Na, K, Ca, Sr, Pb, Cu, and Fe on the obtained results. The absolute detection limits achieved were in the range of 10^{-8} to 10^{-11} g. Effects of various instrumental and chemical conditions on the Ru emission signals were studied using a laminar air-acetylene flame.[307]

The use of plasma as excitation source provides better sensitivity (ppb levels) of the results. The determination of ruthenium freedom from the other noble metal interference was reported using a radio-frequency (2 kW) inductively coupled plasma source.[308] No effects from 10-fold excess of Cu, Fe, Ni, and Zn were observed. Mineral acids depressed the emission intensity of Ru (as well as the other noble metals) due to variation in the uptake rate and efficiency of the nebulizer system with change in the density and viscosity of the solutions aspirated. Sulfuric acid at 10% concentration decreased the signal of Ru by 27%. Hydrochloric acid gave the lowest interfering effects. The interference from Ru (265.96 and 442.08 nm lines) on the Pt (265.95nm) and Os (442.05 nm) signals, respectively, was investigated.

Periodic acid enhances the ICP AES results for Ru.[309] The DL of 5 ng ml^{-1} Ru (λ = 240.272 nm) was reported. Reducing agents interfere with the determination of ruthenium. Sodium at concentration above 0.01 *M* suppresses the emission intensity of Ru (similarly to the other noble metal signals).[310] The suppressing effect was found to be independent of analyte concentration, but was enhanced by an increase in acid concentration. No effect of Na on the excitation temperature or electron density of the plasma was observed. A 400- to 10,000-fold excess of Ca, Mg, Fe(III), Al, Zn, Ni, Cu(II), Mn(II), and Zr(IV) hardly caused interferences in the determination of Ru (Au, V and Ti) separated by the use of poly(epoxy)melamine chelating resin.[311]

The AES detection was employed to determine Ru (0.044% to 0.49%) and the other noble metals in alloys after oxidation decomposition of the samples under the action of potassium tetrafluorobromate followed by the conversion of complex fluorides obtained into soluble chloride complexes ($K_4Ru_2OCl_{10}$ for ruthenium) in the presence of HCl.[312] The results were compared with those obtained by AAS technique.

Attempts to use ICP AES with electrothermal vaporization to the determination of Ru (used as chemotherapeutic agent) in human body fluids were described.[313] DL of 19 ng ml^{-1} (95 pg) for Ru was reported.

Spectrographic determinations of ruthenium and the other PGM after their preconcentration by precipitation with thiourea and adsorption on activated carbon[314] or extraction with diantipyrylthiourea ($CHCl_3$)[152] were described. The DL of 10 ng g^{-1} and 4.0 to 300 μg Ru, respectively, were reported. Preliminary separation of Cr by distillation was employed to determine ruthenium in ore samples of high Cr content.[314]

Detection limits not greater than 10^{-7}% (50 g sample) were reported for simultaneous spectrographic determination of all noble metals in one sample of various copper nickel industrial products after fire assay digestion of the samples, vacuum distillation of the lead matrix, decomposition of the residue in conc. HCl and preconcentration on a POLYORGS IV sorbent.[93]

E. Inductively Coupled Plasma Mass Spectrometry

Multielement capabilities and excellent detection limits offered by inductively coupled plasma mass spectrometry make the technique the most promising for the determination of ultra-traces of noble metals in a large variety of complex matrices.[4,5,315,316] Lower, when compared with the other instrumental techniques, concentration levels of the metals can be determined in shorter period of time. The need to prepare sample solutions containing low concentration of dissolved solids and to eliminate isobaric interferences from polyatomic ions are the main limitations in the range of applications of the technique. Monitoring the contamination from chemicals, vessels and laboratory air requires special attention to maintain low procedural blank. Application of isotope dilution (ID) technique for quantifying the analytes is an attractive approach to compensate the effects of interferents. Electrothermal vaporization (ETV), laser ablation (LA) and ultrasonic nebulization (USN) as alternative to solution nebulization sample introduction technique are applied to extend the analytical range of ICP MS measurement in terms of detection power and increase the scope of applications.

A number of matrix and isobaric interferences, including those from Mo (^{96}Ru); Mo (^{98}Ru); Mo and ^{84}Sr^{16}O (^{100}Ru); ^{84}Sr^{16}O^{1}H, ^{61}Ni^{40}Ar and ^{64}Ni^{37}Cl (^{101}Ru); Pd and ^{86}Sr^{16}O (^{102}Ru) can affect the ICP MS ruthenium signal. Separation steps often precede the detection of the metal. Ruthenium is usually determined simultaneously with the other noble metals while present in the examined sample. The preconcentration of the metal is needed in analysis of samples of lower concentration than the DL available.

The combination of ICP MS technique with nickel sulphide FA provides the highest recovery of all noble metals from a large number of geological samples, *e.g.,* rocks, ores, and minerals.[101,104,317–320] Dry chlorination[87,321] and alkaline oxidation fusion[85,191] are also used. Detection limits in low pg levels (0.2 to 0.5 ng g^{-1}) have been reported. The 90±10% recoveries for Ru (within the 20 to 780 ng g^{-1} range) (as well as Pd, Ir, and Pt) in geological samples were achieved when employing alkaline fusion digestion, anion-exchange pre-concentration and ID ICP MS detection. The ICP MS technique was used to check the recovery of precious metals from certified reference materials: SARM 7 (430 ng g^{-1} Ru); CHRPt+ (9.2 μg g^{-1} Ru) and CHR-Bkg (67 ng g^{-1} Ru) using the three sample pre-treatment steps: nickel sulfide FA, lead FA and aqua regia leaching.[104]

The ETV-ICP MS detection of Ru (Pt, Pd and Ir) at ppb levels in ultramafic rock samples provides a 50% increase in sensitivity as compared with solution nebulization.[318] Nickel (500 ppm Ni as nitrate) can be used as a matrix modifier. The effect of Ni on the analyte signals for solution nebulization and ETV was examined. Detailed studies on the mechanism by which the PGM are vaporized in the graphite furnace were described.[297]

The monitoring of ^{99}Ru and ^{101}Ru isotopes has been used to determine ruthenium in photographic materials, emulsions (~100 mg g^{-1} Ag) and films (~2 g m^{-2} Ag), by ETV-ICP MS technique.[322] Minimal sample pre-treatments employing the dissolution of the examined sample in warm water (40^{0}C) or 0.14 *M* HNO$_3$ (for liquid sampling) or drying at 105^{0}C (for solid sampling) were applied. On-line separation of silver from Ru (as well as from Rh and Ir) by using the appropriate heating programme was possible. It has been found that silver starts to volatilize at temperature of about 1000^{0}C, while Ru, Rh and Ir are volalilized at temperature of about 1500^{0}C or higher. About 90% of Ag matrix can be removed prior to volatilization of ruthenium by applying multisteps heating programme. The results for Ru (*ca.* 1 μg Ru per g Ag) were in good agreement with those obtained by pneumatic nebulization ICP MS and/or ETAAS. The use of Ir as internal standard has been recommended to correct for signal suppression due to residual matrix effects and to improve the precision of measurements.

The ID ICP MS with silver matrix separation by AgCl precipitation has also been proposed for the determination of ruthenium traces in photographic emulsions (0.1 to 10 μg Ru per gram emulsion).[323] Losses of ruthenium by co-precipitation with AgCl have no effect on the results. The ^{99}Ru spike solution was applied.

Attempts to determine ruthenium (and the other noble metals) in geological materials by ultraviolet LA ICP MS technique followed the nickel sulfide FA have been described recently.[319,320] Detection limits of 3.5 ng g^{-1} Ru[319] and 5 ng g^{-1} Ru[320] were reported. Good agreement was observed between the examined and reference material.

Ultrasonic nebulization sample introduction has been examined for quantifying Ru (and the other noble metals) in geological samples using cation-exchange preconcentration.[324] Concentration ranges determined and detection limits were in low pg g^{-1} and fg g^{-1} range, respectively. Mass spectrometry with negative thermal ionization was applied to accurate measurement of ruthenium isotopes[325] and the atomic mass of ruthenium.[326]

The ICP MS technique was applied to the determination of ruthenium (1.223 μg ml^{-1} and 0.0552 μg ml^{-1}) in fission product in spent nuclear fuels (with enriched ^{96}Ru isotope as a spike),[327] in small amounts (2 to 20 mg of the examined samples) of sulfide and oxide minerals (DL of 4 ng g^{-1}),[196] in sulfide inclusions of Fe and Ni-rich sulfides within crack-free natural diamonds (DL 15 pg ml^{-1} Ru)[328] and in volcanic fluids.[329]

On-line electrospray mass spectrometry has recently been used for examination of photosubstitution of (polypyridine)ruthenium(II) complexes and for the determination of reaction intermediates.[330] The kinetics of some Ru metallodrugs binding to human serum proteins has recently been studied by ICP MS coupled to size-exclusion HPLC.[229] The ICP MS technique was used to check the chromatographic behaviour of precious metals (among them ruthenium) on Dowex 1-X8 resin[190] and their preconcentration on midified silicagel.[331]

F. X-Ray Fluorescence

The X-ray fluorescence technique exhibits numerous attractive analytical features such as nondestructive nature, both qualitative and quantitative analysis of multicomponent samples, high speed, simple sample preparation and the determination of analytes in a wide concentration range and in a large variety of samples, *e.g.*, metals, alloys, powders and solutions. The technique can be directly applied to the determination of elements at concentration levels from $n \cdot 10^{-4}\%$ to 70 to 80%, or to the detection of lower analyte contents employing preliminary separation and preconcentration steps. The requirement for standards with the same chemical composition and physical properties narrows direct application of the technique in analysis of real samples.

XRF is widely applied in analysis of a large variety of noble metal samples such as alloys, minerals, industrial products, high purity metals and numerous compounds.[332–335] The majority of methods developed for ruthenium use $K_{\alpha 1}$ line owing to high intensity and relatively low interferences. Dilution methods, internal standards or mathematical correction are used to eliminate matrix effects on the Ru signal.

The effects of base metals on XRF signal of Ru have been examined.[179,184,195,333,336] The reduction of the Ru signal by 10% was observed in the presence of 200 μg Ni or Cu (DL 1 μg Ru).[333] The application of background correction in XRF analysis of solutions used in nonferrous metallurgy containing Ru, Pt, Pd, Rh and numerous base elements has been described.[336]

Separation and preconcentration steps are used to eliminate the interference from major constituents of the examined samples and to determine ruthenium at concentration levels below the DL offered by the technique. The main procedures of sample preparation steps in analysis of materials of various compositions and origin were considered.[335] Sorption methods are favourite to precede the XRF detection of ruthenium. Pre-concentration of ruthenium and the other noble metals on poly(thioether)[179] and polymeric sorbent containing tertiary amino-nitrogen[184] prior to the detection by XRF in solutions containing large proportions of Cu, Ni, Co, and Fe was described. Complete recovery of Ru (≥ 80 μg Ru) from 1 to 10 M HCl solutions containing 10 mg ml^{-1} of base metals[179] or any amounts of Ni and Co, ≤ 40 mg ml^{-1} Cu and ≤ 80 mg ml^{-1} Fe[184] was achieved. XRF combined with an anion exchange paper was successfully applied to the determination of 10 to 100 μg Ru (and Os) in solutions containing 300 mg Cu, Fe, and Ni.[195]

The effect of the other PGM on the intensity of Ru line was investigated.[179] Mutual effects of the noble metals can be neglected during the detection of all metals in the concentration range from 7 to 300 μg g^{-1} while using preliminary concentration of the analytes on fibrous material coated with the finally dispersed sorbent POLYORGS X1-H containing benzimidazole groups.[337] The polymer matrix did not affect the analytical line intensities.

Ruthenium (and Ir) at concentrations > 4 ppm (and Pt, Pd and Rh (> 7 ppm)) in technological solutions containing < 5, 3, 1, 8, 4.5, 2, 0.4 and 0.4 g l^{-1} of Zn, Cu, Ni, Fe, Te, Se, Bi, and Pb, respectively, was determined using Cd and Ga as internal standards.[338] Interelement effects were corrected by a multiregression methods. XRF exhibited the best choice for the determination of ruthenium in electrochemical anodes coated with ruthenium dioxide.[339] The effect of tin on the results for Ru using americium-241 excitation source was investigated.

The XRF technique has been applied to the determination of Ru state in Ru/Al_2O_3 and Ru/SiO_2 catalysts.[340] Complete oxidation of Ru to RuO_2 was established under heating the catalysts in the oxygen atmosphere. Binuclear $(Al_2O_3)RuO_2$ oxides were identified on the surface of Ru/Al_2O_3 catalysts.

Ruthenium in the concentration range from 0.01 to 0.04% has been determined in ten different materials using the equations for the evaluation of the XRF data.[341] Stability of XRF ruthenium signals for complexes of different composition ($Na_2[Ru(NO)(NO_2)_4OH]$ and $(NH_4)_2[RuNOCl_5]$) has been investigated.[342]

The DL of 0.003 ppm for Ru (Rh and Pd) in rocks and ores (0.4-1 g of speciment) was achieved by application of synchrotron radiation XRF technique.[343] Earlier, the DLs of 0.017 to 0.07 ppm of the metals in silicate rocks, ores and reference materials were obtained.[344] Detection limit of 3 ng g^{-1} Ru, Pd and Rh in ores (0.1 to 1 g samples) was reported.[345] Ruthenium (Pt, Pd, Fe, and Cr) in corrosion-resistant steels was determined by using a thin-film technique.[346] Laser atomic fluorescence spectroscopy with vacuum electrothermal atomization was applied to the determination of ruthenium in metal samples.[347] The DL of $1 \cdot 10^{-7}\%$ in copper and lead beads was reported.

G. Neutron Activation Analysis

Neutron Activation Analysis is particularly suitable for the determination of trace quantities of noble metals owing to high sensitivity offered, freedom from contamination and accuracy. The analysis employs the production and detection of specific radionuclides of the element determined. The determination of ^{96}Ru and ^{102}Ru is preferred due to the suitable half-life of their (n,γ) reaction products and large activation cross sections.

Direct application of NAA in analysis of real samples is limited due to interferences from complex matrices. The interfering effect can be critical in the determination of extremely low concentrations of the analytes while long irradiation time is required. Homogeneity of the examined materials may strongly affect the precision of the results.

Numerous radiochemical NAA methods, employing separation and preconcentration of ruthenium from a large variety of samples, have been developed.[106,108,348–357] Fire assay pre-concentration, ion-exchange chromatography, sorption, and co-precipitation with a suitable collector are most often combined with NAA.

The methods for determining Ru (and the other noble metals) in geological materials using NiS FA pre-concentration have been described.[106,108,353] Detection limit of 0.5 ppb Ru was reported when employing the combination of FA and sorption on polyvinylbenzylmethylpyrazole.[106,108] Radiochemical NAA using solvent extraction of RuO_4 by CCl_4 was applied to determine Ru in geological and technological samples.[351] The organic phase was submitted to γ-ray spectrometry for ruthenium determination. Ruthenium in ores and catalysts was determined by NAA involving substoichiometric solvent extraction with 2-thiobenzothiazole into $CHCl_3$.[352] ^{103}Ru produced by the (n,γ) reaction on ^{102}Ru with thermal neutrons allows to determine Ru with DL of 0.099 μg.

Selective group absorption of the analytes on ion-exchange resins (Seelex G and Srafion NMRR) following irradiation of the samples was applied to determine all noble metals in rocks, ores, minerals, lunar samples, coal, coal fly ash, and biological materials.[348] Ruthenium was determined through its two isotopes ^{97}Ru after 2 to 3 days' decay or ^{103}Ru after 15 days' decay. The 30 to 40% precision of the results was reported.

Low levels of radioruthenium in foodstuffs (30 to 120% recoveries of ^{106}Ru) were determined using AG 1-X8 anion-exchange separation.[355] Ruthenium (1.090±0.200 ppm) (Pt and Os) in copper samples was determined by NAA with a preconcentration procedure using a cation-chelating resin.[350]

Simple carrier-free methods have been developed for the determination of ruthenium in urine.[354,356] *In situ* reaction of ruthenium tetroxide, obtained after distraction of the organic matter and oxidation of ruthenium with potassium periodate, with polyethylene powder makes the basis of the determination. Recovery of ^{106}Ru was found to be above 80% by counting β-activity of the prepared samples.

Radiochemical NAA was used to determine noble metals, including Ru, in geological samples of varied compositions (Si and Cr enriched) employing co-precipitation with Se.[349] The technique was applied to determine the isotopic abundance ratio of $^{106}Ru/^{102}Ru$ in meteorites.[357] Experimental factors such as sampling, irradiation, separation and counting that can affect the isotopic ratio were discussed.

A non-destructive procedure for the determination of all PGM and the other siderophilic elements in meteorites using various irradiation and decay times and selecting γ-rays was developed.[358] The determination of Ru and the other components of the RuO_2, $Ru_{1-x}M_xO_2$ (where M is Nb, V), $Pb_2Ru_2O_6$, $PbNbRu_2O_{6.5}$, $Bi_2Ru_2O_7$, and $BiNbRu_2O_7$ compounds by a nondestructive method has been described.[359]

Background levels of Ru and the other noble metals in plants were determined by instrumental NAA.[360] The DLs obtained were compared with those achieved using preconcentration technique, dry ashing, fire assay and post irradiation separation of the analytes employing Srafion NMRR ion-exchange resin. Instrumental NAA analysis of a Ni-S FA button was applied to determine ruthenium and the other noble metals in ore.[99] The DL of 200 μg kg^{-1} Ru in Cu-free samples was reported.

Ruthenium was one of the elements determined in Pt-rocks by neutron irradiation of the samples followed by γ-ray spectrometry.[361] Activation determination of all PGM, Ag and Au (at the level of $n \cdot 10^{-7}\%$) with the use of high-energy protons has been examined recently.[362]

Nuclear interferences from uranium[363,364] and thorium[365] fission products with the determination of Ru (and the other elements) by NAA under various irradiation conditions were examined.

H. Catalytic Kinetic Methods

Catalytic effect of ruthenium on the oxidation of some organic substances by various inorganic reagents, *e.g.*, IO_4^-, H_2O_2, BrO_3^-, hexacyanoferrate(III), as well as the redox reactions in the systems containing inorganic oxidant and reductant (most often IO_4^-, Ce(IV) and As(III)) makes the basis of kinetic methods. Low detection limits (ppb and sub-ppb levels) are the main advantages of the developed methods.

The catalytic activity of ruthenium depends on its chemical form in the examined solution. Ruthenium(III) and Ru(VIII) exibit the highest catalytic activity. The transformation of the metal into a suitable oxidation state is required prior to the detection. Poor selectivity of catalytic methods strongly restricts their application to analysis of real samples. The determination of Ru is usually carried out in pure solutions obtained after its preliminary separation by distillation.

Catalytic effect of ruthenium on the oxidation of 4-(*N*-methylanilino)-benzenesulphonic acid[366] and Acid Orange[367] by KIO_4 makes the basis of the determination of ruthenium in the concentration ranges of 0.05 to 0.5 ng ml^{-1} and 0.003 to 10 μg g^{-1}, respectively. The applications of the methods in analysis of ore samples and copper alloy have been reported. Ruthenium in ammino, hydroxy, carboxycoumarin complexes, and carbon catalysts was determined by the use of oxidation of 4-(*N*-methylanilino)benzenesulphonic acid with ammonium vanadate (DL $4{\cdot}10^{-11}$ g ml^{-1}).[368] Catalytic determinations of ultratrace amounts of ruthenium employing the redox reaction between Rhodamine B (1 to 30 ng Ru)[369] or malachite green (DL 0.3 ng l^{-1})[370] and KIO_4 have been reported. Detection limits of 3 pg ml^{-1} (ore samples)[371] and < 1 μg g^{-1} (concentrates)[372] have been achieved by monitoring the kinetics of the reactions of Methyl Red and carboxyarsenazo with KIO_4, respectively. The oxidation of haematoxylin by H_2O_2,[373] Thymol Blue by BrO_3^-[374] and benzylamine by hexacyanoferrate(III)[375] catalyzed by Ru(III) allows the determination of the metal in concentration ranges of 5 to 150 ng ml^{-1}, 0.001 to 0.025 μg ml^{-1} and 10 to 121 ng ml^{-1}, respectively. Flow injection system has been used to determine ruthenium (up to 0.12 g ml^{-1}) on the basis of the catalysis of the periodate oxidation of the 1,10-phenanthroline-Fe(II) complex in the presence of perchloric acid.[376] The determination of ruthenium in sulfato complexes has been accomplished on the basis of its catalytic effect on the oxidation of diphenylamine with periodate (DL 0.05 μg ml^{-1}).[377]

Catalytic oxidation of Tropaeolin OO with KIO_4 has found applications to the determination of ruthenium directly in solutions obtained after digestion of the examined samples, *e.g.,* in copper-nickel sulfide ($2{\cdot}10^{-6}$ to $1{\cdot}10^{-4}$ μg ml^{-1} Ru),[378] in copper alloys and some technological[379] and industrial[380] materials, and in sulfate process solutions.[381] Catalytic reaction of Tropaeolin OO with KIO_4 has also been applied to determine ruthenium in sulfide, silicate and oxide ores, biogeochemical materials and natural waters[382] as well as in Fe-Mn concentrates (no interference from Au, Cu and Ni in 10^5-fold or Fe and PGM in 10^3-fold molar excess).[383] Detection limit of 10 ng Ru in 2.5 ml of the examined solutions has been reported.[384]

The elimination of interferences from common metals in the catalytic determination of ruthenium by the use of a cation-exchange (KU-2 resin in H^+ form) separation steps prior to the detection has been described.[385,386] Rapid tests for the determination of sub-microgram amounts of ruthenium have been proposed using the catalytic reaction of *o*-dianisidine with Ce(IV) (DL $2{\cdot}10^{-5}$ μg Ru).[387] The majority of accompanying non-ferrous and heavy metals do not interfere with the developed tests.

Methods for simultaneous determination of ruthenium and osmium based on their catalytic effects on the reaction between Ce(IV) and As(III) have been described.[388–390]

Spectrophotometry is most often used for monitoring the rate of catalytic reactions. Polarographic methods based on catalytic currents recorded are also used.

Precision, accuracy, and quickness of different kinetic methods for the determination of PGM, including Ru, have been compared to express control of technological processes.[391] Review article on the kinetic methods for the determination of ruthenium has been published.[392]

I. Electrochemical Methods

Numerous electrochemical methods have been developed for the determination of noble metals. Alternating current polarography, differential pulse polarography, adsorptive stripping voltammetry, and coulometry have found the widest application for determining ruthenium. Standard and formal potentials, half-wave potentials and current peak maxima of reduction and oxidation redox systems useful in analytical procedures have been generalized.[393]

Polarographic methods are based on catalytic waves in the presence of complexing agents, *e.g.,* quinoline-8-thiol[157] or quinoline-8-ol.[394] Complexes with quinoline-8-thiol make the basis of the determination of ruthenium (Os and Ir) in a copper-nickel sulphide ore and a concentrate (DL 0.22 μM Ru) by alternating current polarography.[157] No interference was observed from Pt, Rh, Au, Ag, Ni or Cu while using the preliminary extraction of the analytes with quinoline-8-thiol into molten naphthalene. A differential pulse polarographic method for selective determination of ruthenium (DL 1 ppm) in the presence of Rh employing extraction pre-concentration of quinoline-8-olates on microcrystalline naphthalene has been proposed.[394] Mutual electrochemical interference of both elements caused by their close peak potential was overcome by the control of pH and digestion temperature.

The polarographic behaviour of 3-thiopropionic acid as a reagent in the amperometric titration of Ru(III) was examined.[395] Serious interferences from the other PGM were observed. Differential amperometric titration method for the determination of ruthenium(VI) (0.2 to 15 mg Ru) in mixtures with Os(VI) (1:3 to 4:1), Pd(II) (1:4 to 5:1), or Ag (1:5 to 5:1) has been developed.[396] The determination of particular components can be accomplished by a single titration (the titration curves exibit two distinct end-poits).

A sensitive method (DL 0.003 μg ml^{-1} Ru) based on the catalytic current of the Ru(III)-bromate system on the surface of a hanging mercury electrode has been described.[397] Ruthenium in the concentration range of 5 to 80 ng ml^{-1} was determined with the use of a hanging mercury drop electrode in the presence of acetate buffer, $NaClO_4$ and ethanolic salicylaldehyde thiosemicarbazone (2:2:1).[398] Interference tolerances for 21 metals ranged from equimolar (Rh) to > 100-fold (Fe, Mn, Mo, Ni, and Zn). The sensitive method for the determination of ruthenium (DL $8 \cdot 10^{-8}$ M) in the presence of Rh in a copper-nickel sulfide ore has been developed.[399]

Adsorptive stripping voltammetry offers high sensitivity for ruthenium. Adsorptive accumulation of the complex of ruthenium (and Pt) with 1-(2-pyridylazo)-2-naphthol on the surface of hanging mercury drop electrode followed by the reduction of the absorbed complex during the cathodic scan makes the basis of extremely sensitive method (DL $5.1 \cdot 10^{-10}$ M Ru).[400] Detection limit of 2 nM Ru was reported while using adsorptive accumulation of the analyte in the presence of hydrazine in acidic acetate buffer.[401]

Cyclic voltammetry has been used to investigate electrochemical properties of Ru(III)/Ru(II) chloro carbonyl[402,403] and chloride Ru(IV)/Ru(III)[54] complexes and to characterize the incorporation of three ruthenium complexes: *tris*(2,2'-bipyridine)-ruthenium(II), *tris*(1,10-phenanthroline)ruthenium(II) and *bis*(2,2'-bipyridine)1,8-naphthyridine-ruthenium(II) into a Nafion polymer-modified glassy carbon electrode.[404]

Voltammetry was employed to determine ruthenium in complexes with biologically active *N*-containing ligands, *e.g.,* imidazole and histamine,[405] in semiconductor[406] and in organometallic compositions.[407]

Detailed discussion of voltammetric methods for the determination of PGM (including Ru) has been presented.[408] Different variants of preconcentration in voltammetric methods have been discussed.[409]

Controlled-potential coulometry has shown to provide most effective methods for the determination of ruthenium among the developed coulometric methods.[410,411] Chloride complexes of Ru(IV) and Ru(III) make the basis of the developed procedures.

Oxidation-reduction of dimer chloride complexes of Ru(IV) on a platinum electrode makes the basis of the determination of ruthenium in waste materials (0.1 to 5.5 mg Ru)[412] and resistive pastes.[413] Tenfold mass excess of Pt(IV), Pd(II), Rh(III) did not interfere. Au(III) and Ir(IV) interfered with the detection of ruthenium. A procedure for the determination of ruthenium in the composite resistive pastes based on the use of a redox system of chloro carbonyl Ru(III)/Ru(II) complexes[414] has been proposed. Separation of ruthenium from the matrix was not necessary using the latter method.

Coulometric methods for the determination of Ru(IV) by electrically generated Fe(II) in the mixture of HCl, H_2SO_4 and H_3PO_4 (30 to 80% Ru)[235] and hydroquinone[236] have been developed. The hydroquinone method was applied in analysis of samples containing easily hydrolysed ruthenium pentafluoride.

Coulometry has been employed to investigate the oxidation states of ruthenium in hydrochloric acid media.[56]

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