CHAPTER XII

EXTRACTION-SPECTROPHOTOMETRIC DETERMINATION OF TRACE AMOUNTS OF RUTHENIUM(III) WITH BENZYLDIMETHYLPHENYLAMMONIUM CHLORIDE.

12.a. Introduction:

Spectrophotometric methods for determination of ruthenium in which thiourea$^{469}$ and its derivatives are used as reagents are more or less empirical but can be carried out rapidly and rather simply, and will often serve satisfactorily. Strongly coloured products are obtained when an acid solution of ruthenium salt is heated with thiourea and its derivatives. Osmium also reacts with some of these compounds. Various reagents of this type have been studied qualitatively by steiger$^{470,471}$. Some of the reaction products are only slightly soluble in water, but can be kept in solution by adding alcohol.

Yaffe and Voigt$^{472}$ found that both ruthenium(III) and ruthenium(IV) in perchloric acid solution form the same blue-green chelate complexes with thiourea. Like the closely related compound thiourea, dithioxamide$^{473}$ (rubeanic acid) gives blue reaction products with ruthenium under similar conditions.
Thiocyanate gives a pink coloration with low concentration of ruthenium(III) in dilute hydrochloric acid and can be extracted into butyl alcohol. Blue Ru(CNS)$^{++}$ is reported to form by ruthenium(III) and ruthenium(IV) in perchloric acid medium.$^{474}$

In the presence of hydroxylamine hydrochloride, ruthenium(III or IV) reacts with 1,10-phenanthroline to form yellow trips(1,10-phenanthroline ruthenium(II) ion. Osmium must be absent. The sensitivity of the method is 0.0055 µg Ru/cm$^2$ at 448 nm.

p-Nitrosodimethylaniline$^{476}$ gives a green colour with ruthenium(III) in acetate buffered solution on heating. The sensitivity is high. Osmium and nitrates must be absent.

An insensitive method for ruthenium may be based on its conversion to ruthenate by fusion with potassium hydroxide-nitrate and measurement of the absorbance of the orange-red solution of the melt at 465 nm$^{477}$. Another insensitive method utilizes oxidation of ruthenium to perruthenate with a carefully regulated excess of chlorine and absorbance measurement at 380 nm$^{478}$.

Ruthenium(7.9-53.1 µg) and osmium(7.4 µg) in presence of each other was determined simultaneously using 50% water-dioxane$^{479}$ solution. Maximum absorbance was obtained by heating the mixture for 30 minutes in boiling water bath.
Ruthenium in rocks was determined spectrophotometrically as H₂RuO₂Cl₄ at 480 nm. Beer's law is obeyed for 10⁻⁷-10⁻⁵ g Ru/ml.

Ruthenium(III) was determined spectrophotometrically at 530 nm by reaction with 4,5-diamino-6-hydroxypyrimidine sulphate at pH 3-2. The molar absorptivity is 6.5x10³ l mol⁻¹ cm⁻¹.

Ruthenium(III) was determined spectrophotometrically by Pilipenko et al with phenyl thiourea and diphenylthiourea. The complex formed in hydrochloric acid at 75-80° C was extracted into chloroform. Beer's law was obeyed for 0.28-24 µg Ru/ml at 630 nm. Osmium interfered.

Ruthenium forms complex with α-dithionaphtholic acid at pH 5-6, extracted into chloroform and absorbance is measured at 490 nm. Beer's law is obeyed for 0.05-2.4 µg Ru/ml. The molar absorptivity is 2.36x10⁴ l mol⁻¹ cm⁻¹.

 Gowda and Ramappa developed a spectrophotometric method for determination of ruthenium using thioridazine hydrochloride. The ruthenium complex formed in 1.5 N H₂SO₄ had absorption maximum at 640 nm. Beer's law is obeyed for 0.8-8 ppm ruthenium. The Sandell's sensitivity and molar absorptivity are 0.022 µg/cm² and 4.58x10³ l mol⁻¹ cm⁻¹ respectively.
Ruthenium was determined spectrophotometrically by Singh and Katyal with 5-nitroso-2,4,6-tri-aminopyridine. The molar absorptivity at 510 nm is $1.9 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$.

The 1:2 complex formed between ruthenium and chlorpromazine hydrochloride in 1.5 M $\text{H}_2\text{SO}_4$ absorbs its maximum at 530 nm. The colour is developed fully in 5 minutes with 9-fold excess of the reagent. Beer's law is obeyed for 0.4-12 ppm ruthenium. The molar absorptivity and sensitivity are $4.6 \times 10^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and 0.21 $\mu$g Ru/cm$^2$, respectively.

Datta and Das determined ruthenium(III) and osmium(III) with acetothioacetanilide. The ruthenium complex was extracted into chloroform and absorbance was measured at 420 nm. Beer's law is obeyed for 9-31 $\mu$g Ru/ml.

Ruthenium forms red-coloured complex with promazine hydrochloride in 1.25-2 M $\text{H}_2\text{SO}_4$. The absorbance is measured at 515 nm. Beer's law is obeyed over the concentration range 1.3-11.3 ppm. The molar absorptivity is $7.3 \times 10^3 \text{ mol}^{-1} \text{ cm}^{-1}$.

Reeves et al determined ruthenium using 1-phenyl-4,6-dihydroxy-5-nitrosopyridine-3-carboxylate. The reagent reacts with ruthenium at pH 4-5 after heating for 1 hour at 55°C. The complex absorbs its maximum at 535 nm. The molar absorptivity is $4.2 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$. 
Ruthenium forms a complex with potassium per iodate in 1M alkali. The complex absorbs its maximum at 400 nm. Beer's law is obeyed over the concentration range of 4-40 μg Ru/ml.

Monothiourea-3-nitrophthalic acid reacts with ruthenium to form a complex compound which absorbs its maximum at 598 nm. Beer's law is obeyed for 2-24 μg Ru/ml. The molar absorptivity is 2.9x10³ 1 mol⁻¹ cm⁻¹.

Savotina et al determined ruthenium spectrophotometrically using α-furil mono oxime. The water soluble complex forms, is extractable with chloroform and absorbs its maximum at 555 nm. Beer's law is obeyed for 1-25 μg Ru/ml. The molar absorptivity is 1.6x10⁴ 1 mol⁻¹ cm⁻¹.

Ruthenium was determined spectrophotometrically by reaction with chromeazurol S at pH 3. The solution was heated in a boiling water bath for 90 minutes, cooled and the absorbance was measured at 615 nm. The molar absorptivity is 1.2x10³ 1 mol⁻¹ cm⁻¹.

Kamini et al determined ruthenium spectrophotometrically employing 2-methyl-1,4-naphthaquinone monoxime as a reagent. The 1:2 metal:ligand complex formed after heating for 90 minutes in boiling water at pH 8.2-8.4, was extracted with butyl alcohol, absorbs its maximum at 470 nm. Beer’s law is obeyed for 0.19-3.4 ppm. The Sandell’s sensitivity is 0.0036 μg
Ruthenium was determined spectrophotometrically by extraction of its 1:3:2 complex with 1,10-phenanthroline and thiocyanate from neutral solution containing hydrazine hydrochloride, into chloroform and measuring the absorbance of the extract at 490 nm.495

Ruthenium forms a 1:2:4 ion-association complex with chrome azurol S and CTAB chloride496 at pH 4.6-5.6. The complex absorbs its maximum at 610 nm. Beer's law is obeyed for 0.05-6.47 ppm. The molar absorptivity is 4.4x10^4 l mol^-1 cm^-1.

Roy et al497 used 6-trimethyl-1H-4H-pyrimidine-2-thiol for the spectrophotometric determination of ruthenium(III). The absorption maximum of the ruthenium complex is at 670 nm.

Ruthenium(III) reacts with thiocyanate and hexamethyldiphosphoramide498 in 1.5-2.5 M HCl medium. The solution heated in a steam bath for 6 minutes, cooled, extracted into isobutylmethyl ketone and the absorbance is measured at 570 nm. Beer's law is obeyed for 0.7-13 μg Ru/ml. The molar absorptivity and Sandell's sensitivity are 6.94x10^3 l mol^-1 cm^-1 and 0.001 μg/cm² repectively.

Another method for spectrophotometric determination of ruthenium involves the use of α-furildioxime499. The molar ab-
sorption at 545 nm is \( (1.5-2.2) \times 10^4 \) \( \text{mol}^{-1} \text{cm}^{-1} \).

Basilio Morelli\textsuperscript{500} determined ruthenium using 2-thiobarbituric acid which formed a 1:2 complex (metal:ligand) and absorbed its maximum at 338 nm. The molar absorptivity and Sandel's sensitivity are \( 1.1 \times 10^4 \) \( \text{mol}^{-1} \text{cm}^{-1} \) and 0.0091 \( \mu \text{g} \text{Ru/cm}^2 \) respectively. Gong et al\textsuperscript{501} used 2-(5-bromo-2-pyridylazo)-diethylaminophenol for spectrophotometric determination of ruthenium(III). The red, stable complex formed at pH 3.4-4.0 has a molar absorptivity of \( 1.0 \times 10^4 \) \( \text{mol}^{-1} \text{cm}^{-1} \).

Ruthenium forms a 1:2 complex with 0-mercaptoacetoacetanilide\textsuperscript{502} in presence of \( \alpha \)-picoline as the synergetic agent in the pH range 3.3-6.0. The complex is extracted into chloroform and the extract absorbs its maximum at 585 nm.

Procedures based on formation of ruthenium complex with thiourea and PAR\textsuperscript{503}, 3-chloro-1-nitroso-2 naphthol\textsuperscript{504}, thioridazine hydrochloride\textsuperscript{505}, 6-amino-5-nitroso-2,4-pyrimidine diol\textsuperscript{506}, 2-amino-3-hydroxypyridine\textsuperscript{507}, unithiol\textsuperscript{508} and diphenylguanidine\textsuperscript{509} have been suggested by different workers.

Ruthenium was determined spectrophotometrically by Singh et al\textsuperscript{510} using 3-phenylazo hydroxylamine. The 1:2 metal:ligand complex formed at pH 5-6.5 absorbed its maximum at 535 nm. The molar absorptivity is \( 3.6 \times 10^3 \) \( \text{mol}^{-1} \text{cm}^{-1} \). Sailendra Singh and his co-workers\textsuperscript{511} determined ruthenium using thiosemi-
carbazone. The 1:2 (metal:ligand) complex formed obeyed Beer’s law in the concentration range 2.02-7.09 ppm.

Hayashi et al.\textsuperscript{512} developed a spectrophotometric method for determination of ruthenium(III) using O-diethyldithiophosphate. The red complex formed in hydrochloric acid medium was extracted into chloroform and absorbance was measured at 510 nm. The molar absorptivity is $2.18 \times 10^3$ l mol$^{-1}$ cm$^{-1}$.

Ruthenium(III) after reduction with tin(II) chloride forms RuCl$_2$(SnCl$_2$)$_2$ complex anion\textsuperscript{513} which absorbs its maximum at 445 nm. Beer’s law is obeyed for 0.04-0.2 $\mu$g Ru/ml. The molar absorptivity is $2.71 \times 10^3$ l mol$^{-1}$ cm$^{-1}$.

A 1:6:3 ruthenium thiocyanate-rhodamine 6G ternary complex\textsuperscript{514} in acetate buffer (pH 3-4) is formed which absorbs its maximum at 560 nm. Beer’s law is obeyed up to 5 $\mu$g Ru/25 ml.

Dithiopyrylmethane\textsuperscript{515} reacts with ruthenium and the complex forms is extracted into 6:3 chloroform:isobutanol mixture in presence of perchlorate and ruthenium is determined spectrophotometrically.

Badawy et al.\textsuperscript{516} determined ruthenium spectrophotometrically using halogen derivatives of mono and diphenylazochromotropic acid. Up to 8 ppm of ruthenium could be determined by this method.
Small amounts of ruthenium(III) was determined in Fe-Pt ores spectrophotometrically by Zhilian Jiang$^{517}$ by reaction of ruthenium with potassium per iodate and rhodamine B and measuring the absorbance at 560 nm.

In the present investigation$^{518}$ it has been found that the ruthenium(III)-pyridine-thiocyanate-BDPA complex extractable into 1-butanol and showing absorption maximum at 646 nm can very well be made the basis of a selective and rapid spectrophotometric method for determination of ruthenium in trace amounts.

12.b. Experimental:

(i) Apparatus:

Absorption spectrum of the extracted species over the selected wavelength region was obtained by using a U-3210 spectrophotometer, Hitachi, with matched quartz cells of 1 cm optical path. pH values were measured with an Elico LI-10 pH meter.

(ii) Reagents:

Analytical grade chemicals and solvents only were used.

Standard ruthenium solution:

The stock solution of ruthenium was prepared by dis-
solving 0.3459 g of RuCl$_3$·H$_2$O (Johnson and Matthey, London) in 0.4 M hydrochloric acid and the amount of ruthenium in the stock solution was found out by known method$^{519}$. Solutions of lower concentrations were prepared by appropriate dilution of the stock with distilled water.

BDPA chloride solution:

A 0.05 M solution of benzylidimethylphenylammonium chloride was prepared in distilled water.

Potassium thiocyanate solution:

A 1 M potassium thiocyanate solution in distilled water was prepared.

Other chemicals:

Buffers with pH values in the range 1-2.2 were prepared from 0.2 M hydrochloric acid and 0.2 M potassium chloride. Standard solutions of diverse ions were prepared from sulphates, chlorides or nitrates of metals (in case of cations) and from sodium, potassium or ammonium salts of the species concerned (in case of anions) to study their interfering effect.

(iii) Recommended procedure:

To aliquot of the ruthenium(III) solution containing
0.8-25 ppm of ruthenium, 2 ml buffer with pH 1.3 was added followed by addition of 1 ml potassium thiocyanate, 1 ml BDPA chloride and 2 ml pyridine and the total volume of the aqueous phase was made up to 10 ml with distilled water. The mixture was heated in a boiling water bath for 1-2 minutes, cooled thoroughly under tap water, shaken for 30 seconds with 10 ml 1-butanol, organic layer was separated and dried over anhydrous sodium sulphate. The absorbance of the extract was measured at 646 nm against pure solvent taken as reference.

A standard calibration curve was prepared by plotting absorbances against corresponding ruthenium concentrations. Amounts of ruthenium in unknown solutions were then computed from the standard calibration curve.

The results, which are averages of five determinations in each case, are presented in Table 1.

(iv) Studies on interference caused by foreign materials:

In a separate set of experiments a standard ruthenium(III) solution containing 40.2 μg of ruthenium in each case was mixed with an aqueous solution of one of the foreign species—copper(II), silver(I), gold(III), zinc(II), mercury(II), cadmium(II), lead(II), arsenic(III), arsenic(V), antimony(III), bismuth(III), chromium(III), chromium(VI), molybdenum(VI), tungsten(VI), manganese(II), iron(III), cobalt(II), nickel(II),
rhodium(III), palladium(II), platinum(IV), fluoride, bromide, iodide, oxalate, citrate, tartrate, EDTA, thiourea, cyanide, orthophosphate and acetate in varying amounts without causing significant change in the volume of the aqueous phase to examine its interfering effect. Determination of ruthenium was then completed following the recommended procedure. The tolerance limit was set at that amount of the foreign material for which a recovery of ruthenium with approximately 1 per cent error could be achieved. The upper limit of concentration investigated was, however, restricted to the amount 250-fold excess (w/w) of the ruthenium concentration.

The results showing recovery of ruthenium, and tolerance limits of the foreign species investigated, are given in Table 2.

(v) Experiments on the suppression of interference:

From the results presented in Table 2, it is evident that some ions viz., molybdenum(VI), vanadium(V), antimony(III), bismuth(III), cobalt(II) and nickel(II) have comparatively low tolerance limits. Interference due to molybdenum(VI) and vanadium(V) could be checked by using EDTA as masking agent. Effect of antimony(III) and bismuth(III) were suppressed with iodide. Cobalt(II) and nickel(II) were rendered harmless by complexing them with potassium cyanide.
An aliquot of the ruthenium(III) solution containing 40.2 \( \mu \)g of ruthenium was mixed with an aqueous solution of the interfering ion followed by addition of the masking agent. The determination of ruthenium was then completed following the recommended procedure. Improvement achieved thereby in the tolerance limit and also the amounts taken of the masking agents have been recorded in Table 3.

12.c. Results and discussion:

The greenish-blue coloured complex anion formed between pyridine, thiocyanate and ruthenium(III) ion is completely extractable with 1-butanol when the quaternary salt benzylidimethylphenylammonium chloride is added. The ion-association complex exhibits maximum absorption at 646 nm when measured against the pure solvent as the colourless reagent blank shows no absorbance against pure solvent at 646 nm. Beer's law is obeyed over the concentration range of 0.8-25 ppm ruthenium.

(i) Absorption spectra:

The absorption spectra of the Ru-Py-SCN\(^{-}\) BDPA complex in 1-butanol against pure solvent taken as reference, is shown in Fig. 1. Maximum absorption, as seen from the spectrum occurs at 646 nm. The reagent blank prepared under conditions of the experiment is completely devoid of any absorption at this wavelength.
FIG. 1. ABSORPTION SPECTRUM OF Ru$^{III}$ - Py - SCN$^{-}$ - BDPA COMPLEX.
(ii) Effect of pH:

The effect of pH on colour development was examined by measuring the absorbance of the ruthenium complex in 1-butanol over the pH range 5-7 which results due to the overall addition of hydrochloric acid, potassium chloride buffer and pyridine. The complex exhibits constant and maximum absorbance in the pH range 5.2-6.2 showing a gradual decrease in the value with increase in pH beyond 6.2. If however, the pH of the aqueous layer is lowered below 5.2 then also the absorbance is lower than the maximum value.

The variation of absorbance with pH of the aqueous phase is shown in Table 4.

(iii) Effect of thiocyanate concentration:

The effect of thiocyanate concentration (Table 5) was studied by using potassium thiocyanate solutions of varying concentrations. It was found that addition of 1 ml of 0.1 M potassium thiocyanate (which makes the aqueous phase 0.01 M with respect to KSCN) or 1 ml of 1.5 M potassium thiocyanate (which makes the aqueous phase 0.15 M with respect to KSCN) was adequate for complete colour development. It was observed that concentration below 0.01 M and beyond 0.15 M in the aqueous phase produced low absorbance values. A concentration of 0.1 M with respect to potassium thiocyanate has, therefore, been preferred in the
(iv) Effect of reagent (BDPA chloride) concentration:

It was found that 1 ml of 0.05 M BDPA chloride solution, which make the aqueous phase 0.005 M with respect to BDPA chloride, was adequate for complete extraction of the complex for the given range of ruthenium concentration. At concentration below 0.00125 M, the extraction is incomplete, and low absorbance values are obtained. Increased concentration (up to 0.006 M), however, do not bring about any significant change in the maximum absorbance value.

The results obtained experimentally in respect of reagent concentration are given in Table 6.

(v) Effect of pyridine concentration:

The addition of pyridine to the reaction mixture is mainly to dissolve the precipitate of the ion-association complex formed after addition of BDPA chloride. It may also acts as ligand. Addition of pyridine changes the pH of the aqueous phase which develops after addition of hydrochloric acid and potassium chloride buffer (pH 1-2.2) to 5.2 to 6.2. Addition of pyridine makes the extraction easier and increases the stability of the complex and sensitivity of the method. Pyridine concentration below 15 per cent in the aqueous phase produces low absorbance.
value while higher concentration up to 25 per cent do not bring about any significant change in the maximum value of the absorbance.

Results obtained experimentally in respect of pyridine concentration are presented in Table 7.

(vi) Stability of colour:

The absorbance of the complex $\text{Ru}^\text{III}-\text{Py-SCN}^-\text{BDPA}$ complex in 1-butanol was measured at elapsed intervals of 0.25, 0.5, 1, 2, 3, 4, 6, 8, 10, 12, 14, 18, 22 and 24 hours after extraction at 646 nm against pure solvent. The value was found stable over the period of time investigated. The variation of absorbance with time is shown in Table 8.

The colour intensity of the $\text{Ru}^\text{III}-\text{Py-SCN}^-\text{BDPA}$ complex in 1-butanol under the experimental conditions was independent of temperature change in the range 20-35°C.

(vii) Extraction curve:

For the ruthenium(III) solution which is adjusted to pH 5-6 and is 0.01 M and 0.005 M with respect to potassium thiocyanate and BDPA chloride respectively and 20 per cent with respect to pyridine, a single extraction with 10 ml of 1-butanol with 0.5 minute shaking is sufficient to extract the ruthenium
complex quantitatively. The extraction curve (Fig. 2) shows that quantitative extraction by a single extraction is not possible if the overall pH of the reaction mixture is lower than 5.2 and higher than 6.2.

(viii) Calibration curve sensitivity and precision:

Calibration curve is prepared by the standard procedure. Different known amounts of ruthenium were allowed to react according to the recommended procedure. The absorbance of the coloured extract was measured at 646 nm against the solvent taken as reference. A standard calibration curve was obtained by plotting absorbance values against corresponding ruthenium concentrations (Fig. 3).

The extracted species conforms to Beer's law over the concentration range of 8-250 μg of ruthenium per 10 ml of the extract.

Sandell's sensitivity and molar absorptivity of the method are 0.01209 μg Ru/cm² and 0.8354×10⁴ dm³ mol⁻¹ cm⁻¹ respectively. Though the sensitivity is not very high, the present method is more sensitive than some standard methods for ruthenium, viz., those involving use of thiourea⁴⁶⁹ (sensitivity=0.025 μg Ru/cm²) and diphenylthiourea⁴⁷⁰ (sensitivity=0.028 μg Ru/cm²) as reagents.
FIG. 2. EXTRACTION CURVE OF Ru-Py-SCN-BDPA COMPLEX.
FIG. 3. CALIBRATION CURVE FOR DETERMINATION OF RUTHENIUM.
A standard solution containing 40.2 μg of ruthenium was analysed 10 times according to the recommended procedure. The average absorbance was 0.3323 with a standard deviation of 0.0027 and a coefficient of variation of 0.82%.

(x) Effect of diverse ions:

An examination of the effect of other ions on the determination of ruthenium by the proposed method revealed that copper(II), silver(I), gold(III), zinc(II), mercury(II), cadmium(II), arsenic(III), arsenic(V), chromium(III), chromium(VI), molybdenum(VI), tungsten(VI), manganese(II), iron(III), cobalt(II), nickel(II), rhodium(III), palladium(II), platinum(IV), fluoride, bromide, iodide, oxalate, citrate, tartrate, EDTA, thiourea, cyanide, orthophosphate and acetate are well tolerated in the sense that their presence in an appreciable amount in the reaction mixture does not produce serious harm toward recovery of ruthenium. Molybdenum(VI), vanadium(V), antimony(III), bismuth(III), cobalt(II) and nickel(II) have poor tolerance limits (Table 2).

Tolerance limits of the ions having serious interference were improved by using masking agents (Table 3).

12.d. Application to analysis of synthetic mixtures:

Four different synthetic mixtures were prepared by
mixing solutions of ruthenium(III) with those of cobalt(II), nickel(II), mercury(II), rhodium(III), copper(II), tungsten(VI), chromium(III), palladium(II), molybdenum(VI), manganese(II) and iron(III). The amount of ruthenium present in each sample was then determined by following the recommended procedure. Masking agents were used wherever necessary.

Recovery of ruthenium was excellent conforming to an error less than 1 per cent for 4.02 ppm of ruthenium.

12.e. Conclusion:

The present method for spectrophotometric determination of ruthenium is simple, rapid and sensitive, and yet provides excellent recovery of ruthenium in micro quantities in presence of most of the common ions. Influence of the interfering ions can be easily overcome. The method is, therefore, a selective one. Further, the method is highly precise as shown by the value of standard deviation(0.0027) and coefficient of variation(0.82%) in the absorbance of 4.02 ppm of ruthenium determined. Application of the method to analysis of synthetic mixtures comprising mostly the seriously interfering ions, resulted in satisfactory recovery of ruthenium. The proposed method is thus worthy of finding application for determination of ruthenium whenever a high degree of precision and accuracy are desired.
Table 1

Extractive spectrophotometric determination of ruthenium

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<td>RhIII</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
</tr>
<tr>
<td>PdII</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>2.4</td>
</tr>
<tr>
<td>PtIV</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>0.37</td>
</tr>
<tr>
<td>(1)</td>
<td>(2)</td>
</tr>
<tr>
<td>----------</td>
<td>---------</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>F^-</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>9.0</td>
</tr>
<tr>
<td>Br^-</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>10.5</td>
</tr>
<tr>
<td>I^-</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
</tr>
<tr>
<td>Oxalate</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>9.8</td>
</tr>
<tr>
<td>Citrate</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
</tr>
<tr>
<td>Tartrate</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>2.4</td>
</tr>
<tr>
<td>EDTA</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
</tr>
<tr>
<td>Thiourea</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>0.88</td>
</tr>
<tr>
<td>Cyanide</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
</tr>
<tr>
<td>Orthophosphate</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>8.0</td>
</tr>
<tr>
<td>Acetate</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
</tr>
</tbody>
</table>
Table 3

Suppression of interference

(Ruthenium taken = $40.2\,\mu g$)

<table>
<thead>
<tr>
<th>Interfering ion</th>
<th>Masking agent with amount</th>
<th>Improved tolerance limit (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo$^{VI}$, V$^V$</td>
<td>EDTA (0.5 ml of a 1.0% solution)</td>
<td>0.60</td>
</tr>
<tr>
<td>Sb$^{III}$,</td>
<td>KI (0.5 ml of a 1% solution)</td>
<td>0.10</td>
</tr>
<tr>
<td>Bi$^{III}$</td>
<td>Do</td>
<td>0.60</td>
</tr>
<tr>
<td>Co$^{II}$, Ni$^{II}$</td>
<td>KCN (0.5 ml of 0.2% solution)</td>
<td>0.60</td>
</tr>
</tbody>
</table>
Table 4

Variation of absorbance with pH of the aqueous phase

(The aqueous phase containing 40.2 µg of ruthenium(III) is 0.1M with respect to KSCN, 0.005 M with respect to BDPA chloride.)

<table>
<thead>
<tr>
<th>pH</th>
<th>Absorbance</th>
<th>pH</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td>0.3256</td>
<td>5.8</td>
<td>0.3323</td>
</tr>
<tr>
<td>5.1</td>
<td>0.3289</td>
<td>5.9</td>
<td>0.3323</td>
</tr>
<tr>
<td>5.2</td>
<td>0.3323</td>
<td>6.0</td>
<td>0.3323</td>
</tr>
<tr>
<td>5.3</td>
<td>0.3323</td>
<td>6.2</td>
<td>0.3323</td>
</tr>
<tr>
<td>5.4</td>
<td>0.3323</td>
<td>6.4</td>
<td>0.3296</td>
</tr>
<tr>
<td>5.5</td>
<td>0.3323</td>
<td>6.6</td>
<td>0.3290</td>
</tr>
<tr>
<td>5.6</td>
<td>0.3323</td>
<td>6.8</td>
<td>0.3260</td>
</tr>
<tr>
<td>5.7</td>
<td>0.3323</td>
<td>7.0</td>
<td>0.3207</td>
</tr>
</tbody>
</table>
Table 5

Effect of thiocyanate concentration

[The aqueous phase (pH 5-6) containing 40.2 μg of ruthenium(III) is 0.005 M with respect to BDPA chloride, 20% with respect to pyridine and (x) M with respect to KSCN].

<table>
<thead>
<tr>
<th>Thiocyanate concentration in molarity (x)</th>
<th>Absorbance</th>
<th>Thiocyanate concentration in molarity (x)</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>0.1155</td>
<td>0.08</td>
<td>0.3323</td>
</tr>
<tr>
<td>0.005</td>
<td>0.2174</td>
<td>0.10</td>
<td>0.3323</td>
</tr>
<tr>
<td>0.008</td>
<td>0.3301</td>
<td>0.12</td>
<td>0.3323</td>
</tr>
<tr>
<td>0.01</td>
<td>0.3323</td>
<td>0.15</td>
<td>0.3323</td>
</tr>
<tr>
<td>0.02</td>
<td>0.3323</td>
<td>0.18</td>
<td>0.3215</td>
</tr>
<tr>
<td>0.03</td>
<td>0.3323</td>
<td>0.20</td>
<td>0.3063</td>
</tr>
<tr>
<td>0.05</td>
<td>0.3323</td>
<td>0.25</td>
<td>0.2520</td>
</tr>
</tbody>
</table>
Table 6

Effect of Reagent (BDPA chloride) concentration

(The aqueous phase (pH 5.6) containing 40.2 μg of ruthenium is 0.01 M with respect to KSCN, 20% with respect to pyridine and (y) M with respect to BDPA chloride).

<table>
<thead>
<tr>
<th>Reagent concentration in molarity (y)</th>
<th>Absorbance</th>
<th>Reagent concentration in molarity (y)</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.005</td>
<td>0.3019</td>
<td>0.003</td>
<td>0.3323</td>
</tr>
<tr>
<td>0.001</td>
<td>0.3124</td>
<td>0.004</td>
<td>0.3323</td>
</tr>
<tr>
<td>0.0012</td>
<td>0.3300</td>
<td>0.005</td>
<td>0.3323</td>
</tr>
<tr>
<td>0.00125</td>
<td>0.3323</td>
<td>0.0055</td>
<td>0.3323</td>
</tr>
<tr>
<td>0.002</td>
<td>0.3323</td>
<td>0.006</td>
<td>0.3323</td>
</tr>
</tbody>
</table>
Table 7

Effect of pyridine concentration

(The aqueous phase (pH 5.6) containing 40.2 μg of ruthenium is 0.01 M with respect to KSCN, 0.005 M with respect to BDPA chloride and z per cent with respect to pyridine).

<table>
<thead>
<tr>
<th>Pyridine concentration in per cent (z)</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.3255</td>
</tr>
<tr>
<td>7.5</td>
<td>0.3250</td>
</tr>
<tr>
<td>10.0</td>
<td>0.3271</td>
</tr>
<tr>
<td>12.5</td>
<td>0.3287</td>
</tr>
<tr>
<td>15.0</td>
<td>0.3323</td>
</tr>
<tr>
<td>17.5</td>
<td>0.3323</td>
</tr>
<tr>
<td>20.0</td>
<td>0.3323</td>
</tr>
<tr>
<td>22.5</td>
<td>0.3323</td>
</tr>
<tr>
<td>25.0</td>
<td>0.3323</td>
</tr>
<tr>
<td>27.5</td>
<td>0.3297</td>
</tr>
<tr>
<td>30.0</td>
<td>0.3292</td>
</tr>
<tr>
<td>32.5</td>
<td>0.3267</td>
</tr>
<tr>
<td>35.0</td>
<td>0.3201</td>
</tr>
</tbody>
</table>
Table 8
Variation of Absorbance with time

<table>
<thead>
<tr>
<th>Time in hour</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>0.3323</td>
</tr>
<tr>
<td>0.50</td>
<td>0.3323</td>
</tr>
<tr>
<td>1.0</td>
<td>0.3323</td>
</tr>
<tr>
<td>2.0</td>
<td>0.3323</td>
</tr>
<tr>
<td>3.0</td>
<td>0.3323</td>
</tr>
<tr>
<td>4.0</td>
<td>0.3323</td>
</tr>
<tr>
<td>6.0</td>
<td>0.3323</td>
</tr>
<tr>
<td>8.0</td>
<td>0.3323</td>
</tr>
<tr>
<td>10.0</td>
<td>0.3323</td>
</tr>
<tr>
<td>12.0</td>
<td>0.3323</td>
</tr>
<tr>
<td>14.0</td>
<td>0.3323</td>
</tr>
<tr>
<td>18.0</td>
<td>0.3323</td>
</tr>
<tr>
<td>22.0</td>
<td>0.3323</td>
</tr>
<tr>
<td>24.0</td>
<td>0.3323</td>
</tr>
</tbody>
</table>
### Table 9
Analysis of synthetic mixtures

<table>
<thead>
<tr>
<th>No.</th>
<th>Compositions with amount (in µg) of each constituent</th>
<th>Recovery of ruthenium (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Ru$^{III}$40.2, Co$^{II}$430, Ni$^{II}$480, Hg$^{II}$700</td>
<td>99.8</td>
</tr>
<tr>
<td>2.</td>
<td>Ru$^{III}$40.2, Rh$^{III}$1000, Ni$^{II}$480, Cu$^{II}$1000</td>
<td>99.3</td>
</tr>
<tr>
<td>3.</td>
<td>Ru$^{III}$40.2, W$^{VI}$400, Cr$^{III}$1000, Pd$^{II}$600</td>
<td>99.1</td>
</tr>
<tr>
<td>4.</td>
<td>Ru$^{III}$40.2, Mo$^{VI}$800, Mn$^{II}$850, Fe$^{III}$350</td>
<td>99.7</td>
</tr>
</tbody>
</table>