Zero-Order and First-Derivative Spectrophotometric Determination of Trace Amounts of Ruthenium After Extraction of Its Ion Association Complex With 2,4,6-Tris(2'-Pyridyl)-1,3,5-Triazine and Picrate.

KEY WORDS: Extraction, First-Derivative Spectrophometric, Ruthenium Determination, Ruthenium(III)-TPTZ-picrate complex.

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ABSTRACT

A solvent extraction-spectrophotometric determination of trace amounts of ruthenium has been developed, based on the formation of an ion association complex of ruthenium (III) with 2,4,6-tris(2'-pyridyl)-1,3,5-triazine as primary ligand and picrate as counter-ion; this complex is then extracted into 1,2-dichloroethane. The complex is formed at pH 2.0-7.0, upon heating at 90°C for 60 min, and the ruthenium concentration can be determined by measuring the absorbance directly in the organic phase. Beer's law is obeyed over the concentration range 1.0-10.0 μg ml^{-1} corresponding to 0.050-0.500 μg ml^{-1} of ruthenium in the aqueous solution. The apparent molar absorptivity and the Sandell's sensitivity were found to be $3.4 \cdot 10^5$ l mol^{-1} cm^{-1} and 0.30 ng cm^{-2}, respectively.

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The interference of various ions was examined and the serious interferences from iron and other metals of the VIII group were minimized by employing the derivative spectrophotometric technique in conjunction with appropriate masking agents.

INTRODUCTION

The increasing interest and importance of the use of ruthenium in widely differing fields, such as metallurgy and high technology components, has made it necessary to develop simple, inexpensive and sensitive methods for the determination of trace amounts of this element. There are many spectrophotometric methods for the determination of ruthenium, and except for those that employ heterocyclic azo derivatives [1-4] or sulphur containing compounds [5-9], their low sensitivity make them unsuitable for ruthenium determination at trace levels. Derivative spectrophotometry has opened out possibilities for increasing the sensitivity and selectivity of analytical methods [10-16]. In addition, improvements in sensitivity and selectivity can be achieved by solvent-extraction of an ion-association complex [17-19]. Solvent-extraction is simple, rapid and is most widely used for preconcentration and separation. The extraction spectrophotometric determination of iron and copper as the ternary complexes using phenantroline, 2,4,6-tris(2'-pyridyl)-1,3,5 triazine (TPTZ) and cuproine respectively as primary ligands and picrate as a counter-ion by classical and derivative spectrophotometry has been reported previously [20-22].

In this paper a sensitive and simple method is proposed for the spectrophotometric determination of ruthenium by derivative and zero-order spectrophotometry. The method involves a ternary

system formation in which one of the components is a strongly absorbing molecule (picrate ion) and the other is a chelating ligand containing -N=C-C=N- grouping (TPTZ). The method yields accurate and reproducible results. The derivative technique was used to increase the sensitivity and to eliminate the interference of different ions. When it was not possible, appropriate masking agents were employed.

EXPERIMENTAL

Apparatus

A Shimadzu model UV-160 spectrophotometric with glass cells of 10 mm optical path length was used for absorbance and derivative value measurements.

An Orion Research Digital Ion-Analyzer 701 with glass and saturated calomel electrodes was used for pH determinations.

Reagents

All reagents were of analytical-reagent grade and de-ionised distilled water was used throughout.

Ruthenium (III) chloride stock solution. Dissolve the solid, Aldrich product, in 1 : 20 hydrochloric acid (Merck) and filter. Dilute the filtered solution to known volume with water. Standardize several aliquots of the solution by the method of Banks and O'Laughlin[23]. The resulting solution gives an average of 0.503 g of ruthenium per liter. Prepare the working solutions by dilution.

2,4,6-tris(2'pyridyl)-1,3,5-Triazine (TPTZ) solution, $1 \cdot 10^{-3}$ M Dissolve 0.312 g of the Sigma product in a few drops of hydrochloric acid and dilute to 1000 ml with water.

Sodium picrate solution, $1 \cdot 10^{-2}$ M . Dissolve 2.2911 g of the purified picric acid (Merck) in water, then neutralize the

solution with the standard sodium hydroxide solution using a potentiometric method and then dilute to 1000 ml with water.

Sodium acetate - acetic acid buffer, pH=5.0. Dissolve 164 g of sodium acetate (Merck) in 100 ml of water, add 64.4 ml of acetic acid (Merck) and dilute to 1000 ml with water.

Foreign ion solutions. Solutions of diverse ion for interference studies were prepared by dissolving the calculated amount of each compound (Merck) in order to obtain concentrations of 10-1000 μg ml^{-1} of the particular ion.

1,2-Dichloroethane (DCE) Merck (sp. gr. 1.25).
Ethylenglycol Merck.

Procedure

Add 10 ml of $1 \cdot 10^{-3}$ M TPTZ solution, 1 ml of acetic-acetate buffer (pH=5.0) and 0.5 ml of ethylenglycol to a solution containing no more than 50 μg of Ru (III) and dilute with water to approximately 45 ml and heat the mixture in a water-bath for 60 min at 90 ± 5°C. After cooling transfer the solution into a 250 ml separating funnel, add 4 ml of $1 \cdot 10^{-2}$ M sodium picrate solution and adjust the total volume to 100 ml. Mix and set aside. Shake the mixture for 3-4 min with 5 ml of DCE. Allow the phases to separate and run the organic layer through a cotton fibre into a flask moisture-free. Record the normal spectrum and measure the absorbance of the extract at 510 nm against DCE using 10 mm cells. Obtain the first derivative spectrum from 700 to 400 nm, using $\Delta\lambda$ value between 1.0 to 9.0 nm.

For the preparation of calibration graphs obtain the spectra under the conditions given above for various known amounts of ruthenium in the range 0.050-0.500 and 0.007-0.400 μg ml^{-1} for normal and derivative modes respectively.

Results and Discussion

The reaction between Ru(III) and TPTZ to give a 1:2 binary cationic complex is very slow at room temperature and the absorbance of the complex varies with heating time and temperature, and depends on the water soluble organic solvent added in order to promote the complex formation. This solvent not only plays the role of diluent but also prevents the hydrolysis of the Ru(III). A relatively high and stable absorbance was obtained by heating the reactants, Ru(III) and TPTZ at 90°C in a water bath for 60 min in presence of 0,5 ml of ethylenglycol. However, the molar absorptivity of this binary complex is only $1.44 \cdot 10^4$ l mol^{-1}cm^{-1} and the selectivity for analytical purposes is limited by different cations. We have found that the absorbance and consequently the sensitivity reflected in the magnitude of the molar absorptivity value could be enhanced by adding picrate ion to form an ion-association complex which could be extracted into 5 ml of DCE. Its absorbance is then measured directly in the organic layer at 510 nm. The apparent molar absorptivity, taking into account the effect due to extraction, was found to be $3.40 \cdot 10^5$ l mol^{-1}cm^{-1}. It can be observed that besides the increase in sensitivity by ternary complex formation, there is at least a twenty-fold concentration effect due to the extraction.

Optimum Reaction Conditions

The effect of acid concentration on the formation and extraction of the ternary complex into an organic solvent was investigated at different pH values. The optimum pH range for a constant absorbance was found to be between 2.0 and 7.0. Therefore in subsequent studies a pH of 5.0 was maintained

throughout using an acetic – acetate buffer. The formation of the
ternary complex was examined at temperature ranging from 70 to
90°C. After heating for 60 min at 90°C the absorbance was found
to be constant and remains stable for over one week at
temperature below 15°C. The effect of reagent concentration was
studied by varying the concentration of TPTZ and picrate ion. For
maximum color development 5-10 ml of $1 \cdot 10^{-3}$ M of TPTZ solution
and 3-5 ml of $1 \cdot 10^{-3}$ of picrate solution are required for 10 µg
of Ru(III) per 100 ml of aqueous solution. The addition of large
excess of reagents has no effect on the absorbance.

Several organic solvents were tried for the extraction of
the complex from the aqueous phase. The molar absorptivity was
the highest in DCE and therefore this solvent was selected for
further studies.

Nature of the complex

For the preparation of the picrate derivate complex, a
saturated solution of picric acid was added to the binary complex
obtained. The compound was filtered off and washed with water and
finally dried at 110 °C for 2 hours. The calculated composition
of the $Ru(TPTZ)_2(Picrate)_3$ complex was C=45,98%, H=2,13%,
N=20,86%, Ru=7,17%. The experimental results were C= 46,10%,
H=2,39%, N=20,72% and Ru=7,26%, indicating that the complex has
the following composition $Ru(C_{18} H_{12} N_6)_2 (C_6 H_2 N_3 O_7)_3$. On the
basis of these results its was assumed that the reagent (TPTZ)
behaves as a tridentate ligand given rise to a charged cationic
complex of ruthenium(III) and TPTZ, no oxidation or reduction
having occurred, and that the binary complex reacts with picrate
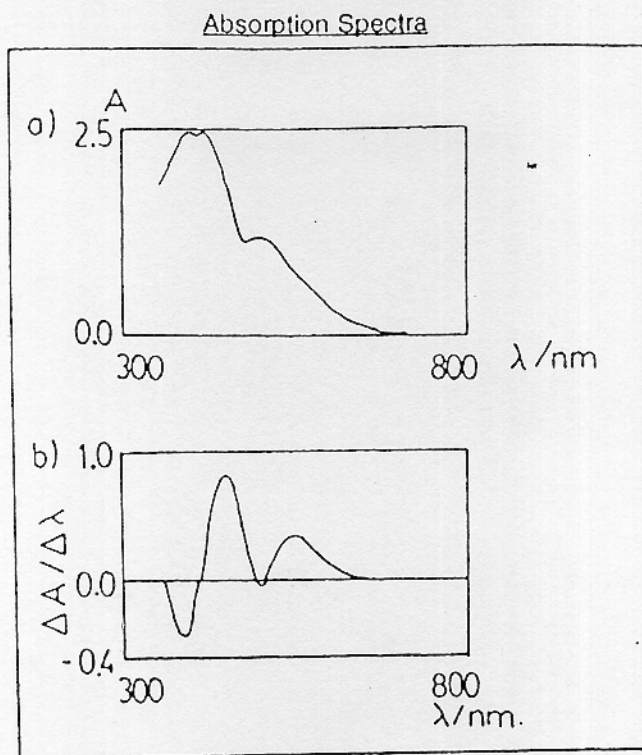ion to give the product above mentioned.

Absorption Spectra

a) A 2.5 ... 0.0 300 800 λ/nm

b) 1.0 $\Delta A/\Delta\lambda$ 0.0 -0.4 300 800 $\lambda/nm.$

Figure 1. (a) Absorption spectrum of DCE extract of the Ru-TPTZ-pic complex measured against DCE. Ruthenium concentration 0,3 µg ml^{-1} in the aqueous phase; all other condition as indicated under Experimental. (b) First-derivative spectrum of DCE extract of the Ru-TPTZ-pic complex measured against DCE. All other condition as in (a).

The figure 1a shows the zero-order absorption spectrum of the Ru-TPTZ-Pic complex extracted into DCE using as reference DCE. The complex shows maximum absorption at 510 nm and this wavelenght was chosen for the determination. At this wavelenght the absorbance depends only on the Ru(III) concentration. The first derivative absorption spectrum of the complex extracted into DCE shows a peak at 520 nm and a valley at 480 nm as is shown in fig. 1b.
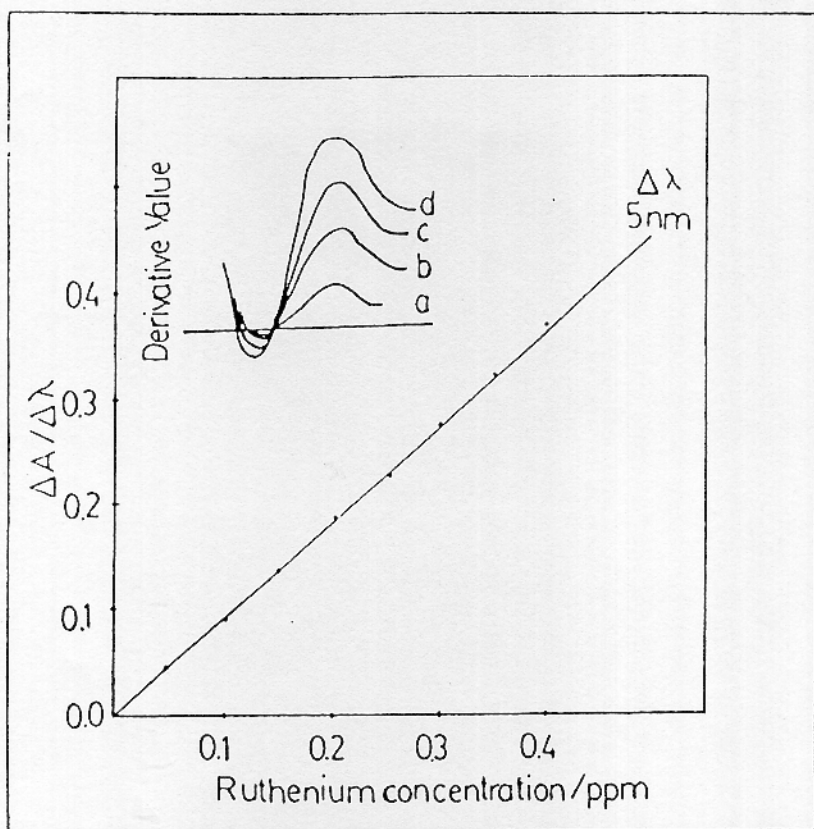
Figure 2. Calibration graph for Ruthenium in First-derivative spectrophotometry. A peak to through values; reference DCE; Aqueous phase ruthenium concentration, μg ml^{-1}. (a) 0.1, (b) 0.2, (c) 0.3, (d) 0.4 ; all other conditions as indicated under experimental.

Spectrophotometric measurements

The absorbance of solutions, containing increasing amounts of the metal ion, was plotted against the metal ion concentration in order to evaluate the range over which the absorbance was proportional to the ruthenium concentration. A good straight line calibration graph passing through the origin was obtained. The equation of the line obtained by the least squarest treatment was [Ru(ppm)] = 0.30 A, where A is the absorbance at 510 nm. The correlation coefficient of the calibration graph was 0.9998. In

the conventional spectrophotometric method the Ru-TPTZ-pic system obeys Beer's law between 1.0 and 10.0 μg ml^{-1} of ruthenium in the organic layer which corresponds to 0.050 and 0.500 μg ml^{-1} in the aqueous phase when V_{aq}/V_{org} = 20. The Sandell's sensitivity and the apparent molar absorptivity were found to be 0.30 ng cm^{-2} and $3.40 \cdot 10^{5}$ l mol^{-1} respectively, as said above. The relative standard deviation for two series of ten solutions each containing 10 and 30 μg of ruthenium per 100 ml was 1.5 and 0.96 % respectively. On the other hand, in the first derivative spectrophotometric method a $\Delta\lambda$ value need to be selected to give better selectivity and higher sensitivity in the determination. A $\Delta\lambda$ of 5.0 nm was selected as the optimum as it gave the best signal/noise ratio. The analytical response was obtained by measuring the distance between the peak at 520 nm and the valley at 480 nm. The calibration graph prepared under the recommended conditions by plotting the derivative value (peak to through value) versus the ruthenium concentration was linear and passed through the origin over the range 14-400 ng ml^{-1} (Fig.2).

The equation for the line following treatment by the least squares method was [Ru/ppb] = 1368 h (r = 0.999), where h is derivative unities. It can be seen that ruthenium can easily be determined down to 400 ng ml^{-1} by the proposed method.

In the absence of interfering ions h is a linear function of original ruthenium concentration in the organic layer and consequently in the aqueous phase. Three series of ten solutions each, containing 20, 100 and 300 ppb, were analyzed. The recovery and the corresponding relative standard deviation values were found to be 19.3 ± 3.9, 100,2 ± 0,56 and 300,1 ± 0,45%, respectively.

Influence of foreign ions on the determination of ruthenium

Few procedures have been published on the determination of trace amounts of ruthenium in the presence of other VIII group metals and other commonly interferent metal ions, Ru usually being determined after isolation by distillation of its tretoxide.

The effect of the presence of foreign ions on the determination of microgram or sub-microgram amounts of ruthenium was investigated by studying the absorption spectra in both the zero-order and the derivative mode.

In spite of the severe interference cause for different metallic cations this interference can be decreased by ternary complex formation when normal spectrophotometry was employed and finally a less pronounced interference was observed when derivative spectrophotometry was used. Table 1 indicates the levels at which different ions can be tolerated depending on the spectrophotometric modes assayed. Because the tolerance for some ions was rather small, appropriated masking agents were used. Table 1 indicates a more pronounced interference when using the normal spectrophotometry. Preliminary assessment indicated a negative interference from the majority of cations examined and serious enhancement from iron (II) and iron (III). That from iron was partially controlled by sodium pyrophosphate which was added after color development. However, large amounts of iron were previously extracted with isobutylmethyl ketone (IBMK) from 6 M Hydrochloric acid and then the pH of the sample was adjusted to the required pH value. It must be stressed that all other masking agents used were added after color development. It was found that the most common anions are tolerated even when present in large amounts.

Table 1.

Influence of foreing ions on the determination of 0.1 µg ml^{-1} ruthenium (III) by normal and derivative spectrophotometry.

Cation added	Normal mode	Derivative mode $\triangle \lambda = 5$nm	Masking agent added ⱡ
Ca(II), Mg(II), Sr(II), Bi(III), Al(II), K(I), Mn(II), Na(I)	1000	1000	------
Zn(II)	800	1000	------
Cu(II)	520	600	------
Ni(II)	400	600	------
Pt(IV)	60	100	------
Pd(IV)	100	200	------
Ir(IV)	80	120	------
Os(III)	160	200	------
Co(II)	100	200	------
	800	1000	EDTA*
Au(III)	10	10	------
	70	100	KBr**
Fe(II)	0	0	------
	500	1000	Na$_4$P$_2$O$_7$***
Fe(III)	0	0	------
	500	1000	Na$_4$P$_2$O$_7$***

ⱡ   Added after colour development.
*   2 ml of $1 \cdot 10^{-1}$ M EDTA solution.
**   0,5 g of KBr.
***   1 gr of Na$_4$P$_2$O$_7$.

Table 2

Determination of Ruthenium in synthetic mixtures by first derivative spectrophotometry

Syntethic mixtures / ng ml^{-1}

Sample	Ru(III)	Pt(IV)	Au(III)	Ir(IV)	Pd(IV)	Co(II)	Cu(II)	Zn(II)	Ni(II)	Fe(II)	Fe(III)	Recovery of Ru/%	RSD /%
1	50	50	50	50	50	50	50	50	50	---	---	100.4	1.4
2	50	100	50	100	100	100	100	100	100	---	---	99.6	1.3
3	50	50	---	---	50	---	---	600	400	---	---	100.6	1.3
4	50	200	50	300	400	---	---	---	---	---	---	100.4	1.4
5	50	---	---	---	400	50	50	50	50	---	---	99.4	1.2
6	50	---	---	---	50	50	50	50	50	500	500	100.4	1.3
7	50	---	50	---	50	50	50	50	50	500	500	99.6	1.2
8	50	50	200	50	50	50	50	50	---	---	---	100.2	1.4
9	50	50	300	50	50	---	---	---	---	---	---	99.6	1.4
10	50	50	50	50	50	400	100	100	100	---	---	100.0	1.2

* Relative Standard Deviation.
I Average of five separate determinations.

Determination of ruthenium in synthetic mixtures.

Samples containing trace amounts of ruthenium were not available. Therefore, synthetic mixtures containing metals of the VIII group and other interferent ions were prepared and the ruthenium content was determined using the proposed method (table 2).

Acknowledgements

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