

## Paper-Electrophoretic Separation of Ruthenium Chloro-Complexes

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### 전기영동에 의한 루테늄 염화착물의 분리

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#### Abstract

Paper electrophoretic separation of octahedrally bonded  $(\text{RuCl}_6)^{3-}$  has been carried out by using the specially designed migration apparatus. The supporting electrolyte solutions are as follows: 0.1 M- $\text{HClO}_4$ , 0.05 M- $\text{HCl}+0.09\text{M-KCl}$ , 0.1M- $\text{HCl}$ ,  $5 \times 10^{-3}$  M-NTA, 0.01M- $\text{HCl}$ , 0.01M- $\text{HClO}_4$ , 0.01M-citric acid, 0.01M- $\text{KH}_2\text{PO}_4+0.01\text{M-Na}_2\text{HPO}_4$ , 0.05M-borax, 0.025M- $\text{Na}_2\text{CO}_3+0.025\text{M-NaHCO}_3$ , 0.01M- $\text{Na}_3\text{PO}_4$ , 0.01M- $\text{NaOH}$  and 0.1 M- $\text{NaOH}$ . The  $(\text{RuCl}_6)^{3-}$  appears in 2 to 4 peaks and is found in several chemical species such as  $(\text{RuCl}(\text{H}_2\text{O})_5)^{2+}$ , cis and trans  $(\text{RuCl}_2(\text{H}_2\text{O})_4)^{1+}$ ,  $(\text{RuCl}_3(\text{H}_2\text{O})_3)^0$ ,  $(\text{RuCl}_4(\text{H}_2\text{O})_2)^{1-}$ ,  $(\text{RuCl}_5(\text{H}_2\text{O}))^{2-}$  and  $(\text{RuCl}_6)^{3-}$ . The retention value has been found to be highest in the 0.025M- $\text{Na}_2\text{CO}_3+0.025\text{M-NaHCO}_3$  electrolyte solution.

#### 요 약

특별히 제작한 영동장치를 써서 8면체 구조의  $(\text{RuCl}_6)^{3-}$ 를 여과지 전기영동 분리하였다. 지지전해질 용액은 다음과 같다. 0.1M- $\text{HClO}_4$ , 0.05M- $\text{HCl}+0.09\text{M-KCl}$ , 0.1M- $\text{HCl}$ ,  $5 \times 10^{-3}$  M-NTA, 0.01 M- $\text{HCl}$ , 0.01M- $\text{HClO}_4$ , 0.01M-시트르산, 0.01M- $\text{KH}_2\text{PO}_4+0.01\text{M-Na}_2\text{HPO}_4$ , 0.05M-붕사, 0.025M- $\text{Na}_2\text{CO}_3+0.025\text{M-NaHCO}_3$ , 0.01 M- $\text{Na}_3\text{PO}_4$ , 0.01M- $\text{NaOH}$ , 0.1M- $\text{NaOH}$ .  $(\text{RuCl}_6)^{3-}$ 은 2-4피크로 나타내며 다음 화학종으로 확인된다.  $(\text{RuCl}(\text{H}_2\text{O})_5)^{2+}$ , cis- 및 trans- $(\text{RuCl}_2(\text{H}_2\text{O})_4)^{1+}$ ,  $(\text{RuCl}_3(\text{H}_2\text{O})_3)^0$ ,  $(\text{RuCl}_4(\text{H}_2\text{O})_2)^{1-}$ ,  $(\text{RuCl}_5(\text{H}_2\text{O}))^{2-}$ ,  $(\text{RuCl}_6)^{3-}$ . 리텐션 값은 0.025M- $\text{Na}_2\text{CO}_3+0.025\text{M-NaHCO}_3$  전해질 용액에서 가장 높다.

#### 1. Introduction

In the processing of nuclear spent fuel, the separation of zirconium, niobium and ruthenium are of difficulty because of their amphoteric nature. In addition, the ruthenium exists in several oxidation states from 0 to +8 and som-

etimes as several species in one oxidation state, and the interconversion reactions are frequently slow. During the dissolution of the spent fuel in nitric acid the ruthenium passes into solution in the form of various nitrato, nitro and mixed nitratonitro complexes of trivalent ruthenium nitrosyls  $(\text{RuNO})^{3+}$ .

The separation techniques of fission products

in liquid state cover precipitation<sup>1,2</sup>, solvent extraction<sup>1,3,4</sup>, ion exchange<sup>5</sup> and electrophoresis<sup>6-9</sup>. Electrophoresis has the advantage of saving the carrier and provides of fractionating the material of spent fuel. In addition, the method is suitable for studies on chemical forms of carrier-free ions in fission products. The migration distance  $L$  of ions is proportional to the product of the potential gradient  $E$  (V/cm) and the migration time  $T$  (sec) as given by

$$L = u \cdot E \cdot T$$

where  $u$  is the mobility (cm/V/cm/sec) of the ion, which is changeable under many migration condition.

By using this technique, halogens, rare-earth, alkaline-earth and alkaline elements have been separated from the other fission products within 20 minutes<sup>7</sup>. The aim of the present work is to separate the chemical species formed in the aqueous solution of ruthenium chloro-complexes in the various pH electrolyte solutions by using a high voltage paper-electrophoresis.

## 2. Experimental

### 2.1. Materials

Carrier free ruthenium-106 (0.6 mCi/ml) as ruthenium chlorocomplex in 4M-HCl solution was obtained from Radiochemical Centre, Amersham, England. The solution was diluted to 0.04M-HCl with distilled water.

A number of electrolyte of different pH values were prepared and the pH value of the solutions thus obtained was measured by a pH meter. Composition and measured pH values of the electrolytes are as follows: 0.1 M-HClO<sub>4</sub> (pH=0.85), 0.05M-HCl+0.09M-KCl (pH=0.9), 0.1 M-HCl (pH=1.1),  $5 \times 10^{-3}$  M-nitritriacetic acid (pH=1.9), 0.01M-HCl (pH=2.0), 0.01 M-HClO<sub>4</sub> (pH=2.2), 0.01 M-citric acid (pH=2.6), 0.01 M-KH<sub>2</sub>PO<sub>4</sub>+0.01 M-Na<sub>2</sub>HPO<sub>4</sub> (pH=6.85), 0.05M-borax (pH=8.5), 0.025 M-Na<sub>2</sub>

CO<sub>3</sub>+0.025 M-NaHCO<sub>3</sub> (pH=10.0), 0.01 M-Na<sub>3</sub>PO<sub>4</sub> (pH=11.7), 0.01 M-NaOH (pH=12.0) and 0.1 M-NaOH (pH=13.2).

### 2.2. Migration Apparatus

Paper-electrophoresis apparatus specially designed for the separation consists of a pair of electrode cells connected with platinum electrodes and a migration cell in which the migration plate is provided. The migration cell, 30×20×4cm, and the cell cover, 30×17×6cm, were made of copper sheet, and the migration plate and the cover plate were duplicated with teflon sheet, 0.3mm in thickness. The migration cell and the cell cover were cooled with ice water by pouring through a hole of 2cm diameter. The electrode cells, migration cell and cell cover were placed into a Lucite container.

### 2.3. Procedure

A strip of Whatman No. 1 filter paper, 40cm long and 1.5cm wide, was wetted with the supporting electrolyte solutions and the excess of the solution in the paper was soaked with another filter paper. The strip was set on the migration plate and its both ends were dipped into the electrode cells containing 300cm<sup>3</sup> each of electrolyte. About ten micro-litre of the sample solution was applied at the fiducial point of the paper strip by using a lambda pipette. The strip was covered with polyvinyl sheets, 31×6.5×0.02cm, and the cell cover was placed onto the migration cell. The electrodes were connected to the D.C. power supply, Toyo model III BA-8, Osaka, Japan, and a potential of 1500 volt was applied for fifteen minutes. After the electrophoresis run was over, the strip was removed from the migration apparatus, dried and cut into pieces of one centimetre length. The radioactivity of each pieces was measured by Nuclear Chicago model 3725 NaI (Tl) crystal well-type gamma scintillation counter.

In the paper-electrophoresis of ruthenium

chlorocomplex under citric acid and borax electrolytes, the cut paper strips were collected together and neutron-irradiated for ten minutes at a thermal neutron flux of about  $10^{13}\text{n/cm}^2/\text{sec}$  by means of a pneumatic tube of TRIGA mark III reactor. The radioactivity of chlorine-38 ( $\gamma$ :2166.8, 1642 keV) in the cut paper strips was analyzed by ORTEC model 7050, 4000 channel pulse height analyzer.

### 3. Results and Discussion

#### 3.1. Error

Since the paper-electrophoresis strips are cut into 1-cm sections, the position of the maximum peak is not fixed accurately. The maximum peak is situated between  $x$  cm and  $(x+1)$  cm at one time or other. Although the paper-electrophoresis was carried out at constant voltage, the voltage fluctuates slightly due to increase of the current density following temperature increase. Therefore, the same chemical species has a migration distance less than  $x$  cm in one experiment and greater than  $x$  cm in another.

#### 3.2. Chlorine/Ruthenium Ratio

The results of the chlorine-38 determination are presented in Table 1. The ratio of chlorine to ruthenium in the paper-electrophoresis species was calculated from the total count rates of chlorine-38 ( $t_{1/2}=37.2\text{min}$ ) and ruthenium-106 ( $t_{1/2}=368\text{d}$ ). Assuming that the ruthenium is octahedrally coordinated and any of the six position not occupied by chloride ions is filled with water molecules, the species are presented as:  $(\text{RuCl}_6)^{3-}$ ,  $(\text{RuCl}_5(\text{H}_2\text{O}))^{2-}$ ,  $(\text{RuCl}_4(\text{H}_2\text{O})_2)^{1-}$ ,  $(\text{RuCl}_3(\text{H}_2\text{O})_3)^0$ , cis- and trans- $(\text{RuCl}_2(\text{H}_2\text{O})_4)^{1+}$  and  $(\text{RuCl}(\text{H}_2\text{O})_5)^{2+}$ .

The ruthenium-106 radioactivity appears in three species on the paperelectrophoresis histogram under ruthenium chlorocomplex-citric acid system. The complex species at -3cm position is assumed to be  $(\text{RuCl}_6)^{3-}$  due to the radioa-

**Table 1. Chlorine/Ruthenium Ratio in the Paper-Electrophoresis Species on Ruthenium Chlorocomplexes**

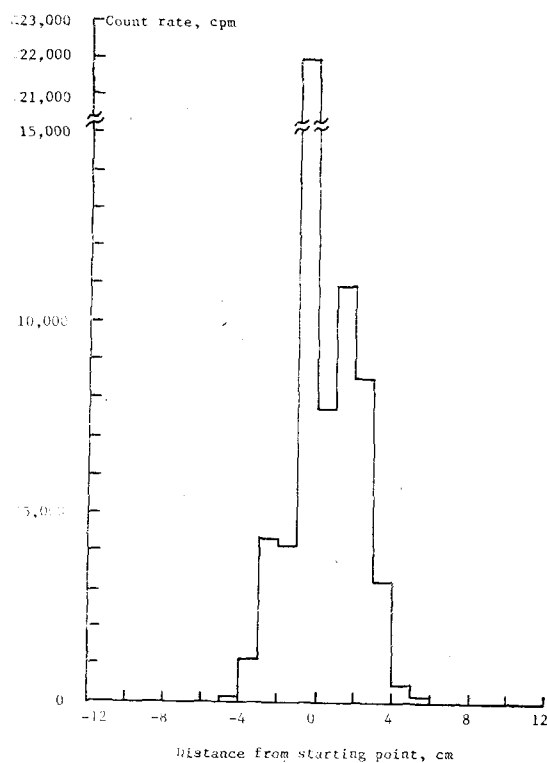
Electrolyte	Migrat-ion distance	Activity, cpm Ru-106	Activity, cpm Cl-38	Cl/Ru ratio
0.01M-citric acid	-3cm	7,715 $\pm$ 87	2,832 $\pm$ 53	0.367
	-1cm	28,275 $\pm$ 168	3,561 $\pm$ 59	0.126
	+2cm	27,420 $\pm$ 165	2,013 $\pm$ 44	0.073
0.05M-borax	-5cm	21,328 $\pm$ 146	3,659 $\pm$ 60	0.172
	-1cm	36,761 $\pm$ 191	3,706 $\pm$ 60	0.101

ctivity ratio of chlorine to ruthenium, that is, 0.367, equivalent to 6 Cl/1 Ru. The complex species at -1cm position remains almost at starting point and gives the radioactivity ratio of chlorine to ruthenium, 0.126 and, therefore, the complex is assumed to be cis- and trans- $(\text{RuCl}_2(\text{H}_2\text{O})_4)^{1+}$  or  $(\text{RuCl}_3(\text{H}_2\text{O})_3)^0$ . The complex species at +2cm position is probably  $(\text{RuCl}(\text{H}_2\text{O})_5)^{2+}$  due to the radioactivity ratio of chlorine to ruthenium, 0.073.

The ruthenium-106 radioactivity appears in two species on the paper-electrophoresis histogram under ruthenium chlorocomplex-borax system. The complex species at -5cm position is assumed to be  $(\text{RuCl}_3)^{3-}$  due to the radioactivity ratio of chlorine to ruthenium, that is 0.172, equivalent to 6Cl/1Ru. The complex species at -1cm position is probably  $(\text{RuCl}_4(\text{H}_2\text{O})_2)^{1-}$  due to the radioactivity ratio of chlorine to ruthenium, 0.101.

#### 3.3. Identification of the Ruthenium Complexes

Typical paper-electrophoresis histograms of ruthenium chlorocomplexes are presented in Figs. 1, 2 and 3. Fig. 1 indicates the paper-electrophoresis histogram of ruthenium complexes under 0.01 M-citric acid electrolyte (pH=2.6). The migrated species are identified according to the determination of the radioactivity ratio of chlorine to ruthenium in Table 1. The similar results of paper-electrophoresis with ruthenium chlorocomplexes under 0.05 M-HCl + 0.09 M-KCl (pH=0.9), 0.01 M-HClO<sub>4</sub> (pH=



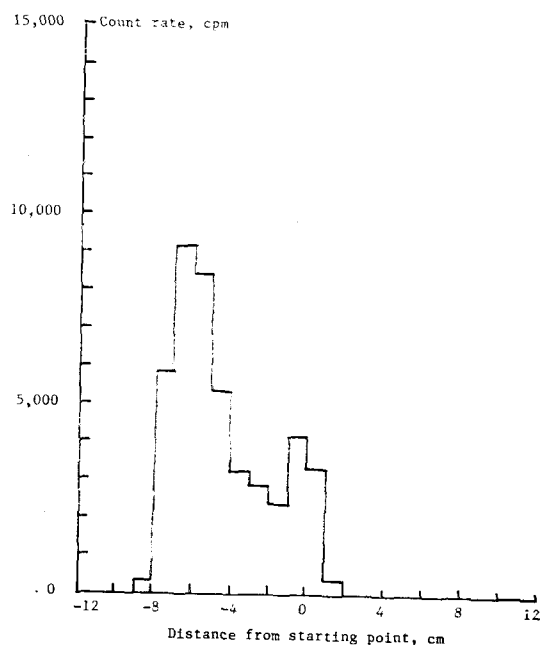
**Fig. 1. Paper-electrophoresis Histogram of Ruthenium Chloro-complexes. Electrolyte: 0.01M-citric acid (pH=2.6)**

0.02 M, 0.01 M-KH<sub>2</sub>PO<sub>4</sub>+0.01 M-Na<sub>2</sub>HPO<sub>4</sub> (pH=6.85) and 0.01 M-Na<sub>3</sub>PO<sub>4</sub> (pH=11.7) are presented:

Electrolyte	Migration distance	Species
0.05 M-HCl+	+4cm	(RuCl(H <sub>2</sub> O) <sub>5</sub> ) <sup>2+</sup>
0.09 M-KCl	+1 to +2cm	cis- and trans- (RuCl <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ) <sup>1+</sup> or (RuCl <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ) <sup>0</sup>
	-4cm	(RuCl <sub>6</sub> ) <sup>3-</sup>
0.01 M-HClO <sub>4</sub>	+5cm	(RuCl(H <sub>2</sub> O) <sub>5</sub> ) <sup>2+</sup>
	+1 to +2cm	cis-and trans (RuCl <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ) <sup>1+</sup> or (RuCl <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ) <sup>0</sup>
	-4cm	(RuCl <sub>6</sub> ) <sup>3-</sup>
0.01 M-KH <sub>2</sub> PO <sub>4</sub>	+2cm	(RuCl(H <sub>2</sub> O) <sub>5</sub> ) <sup>2+</sup>

+0.01 M-Na <sub>2</sub> HPO <sub>4</sub>	-2cm	(RuCl <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ) <sup>1-</sup> or (RuCl <sub>5</sub> (H <sub>2</sub> O)) <sup>2-</sup>
	-5cm	(RuCl <sub>6</sub> ) <sup>3-</sup>
0.01 M-Na <sub>3</sub> PO <sub>4</sub>	+1cm	cis-and trans (RuCl <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ) <sup>1+</sup> or (RuCl <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> ) <sup>0</sup>
	-3cm	(RuCl <sub>5</sub> (H <sub>2</sub> O)) <sup>2-</sup>
	-7cm	(RuCl <sub>6</sub> ) <sup>3-</sup>

Fig. 2 indicates the paper-electrophoresis histogram of ruthenium complexes under 0.025 M-Na<sub>2</sub>CO<sub>3</sub>+0.025 M-NaHCO<sub>3</sub> electrolyte (pH=10.0). In comparison with the histogram under 0.05 M-borax electrolyte, the complex species at -1cm position is assumed to be (RuCl<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>)<sup>1-</sup>. The complex species at -7cm is probably (RuCl<sub>6</sub>)<sup>3-</sup>. The similar results of paperelectrophoresis with ruthenium chlorocomplexes under 5×10<sup>-3</sup> NTA (pH=1.9), 0.01 M-NaOH (pH=12.0) and 0.1 M-NaOH (pH=13.2) are presented:



**Fig. 2. Paper-electrophoresis Histogram of Ruthenium Chloro-complexes. Electrolyte: 0.025M-Na<sub>2</sub>CO<sub>3</sub>+0.025M-NaHCO<sub>3</sub> (pH=10.0)**

Electrolyte	Migration Species	distance
$5 \times 10^{-3}$ M-NTA	-1cm	$\text{RuCl}_4(\text{H}_2\text{O})_2^{1-}$
	-4cm	$(\text{RuCl}_6)^{3-}$
0.01 M-NaOH	+1cm	cis-and trans $(\text{RuCl}_2(\text{H}_2\text{O})_4)^{1+}$ or $(\text{RuCl}_3(\text{H}_2\text{O})_3)^0$ or $(\text{RuCl}(\text{H}_2\text{O})_4(\text{OH}))^{1+}$
	-4cm	$(\text{RuCl}_6)^{3-}$
	-1 to +1cm	$(\text{RuCl}_4(\text{H}_2\text{O})_2)^{1-}$ or $(\text{RuCl}_3(\text{H}_2\text{O})_3)^0$ or $(\text{RuCl}(\text{H}_2\text{O})_4(\text{OH}))^{1+}$
	-5cm	$(\text{RuCl}_6)^{3-}$

Fig. 3 indicates the paper-electrophoresis histogram of ruthenium complexes under 0.01 M-HCl electrolyte (pH=2.0). In comparison with the histogram under 0.01 M-citric acid electrolyte, the complex species at +6cm position is

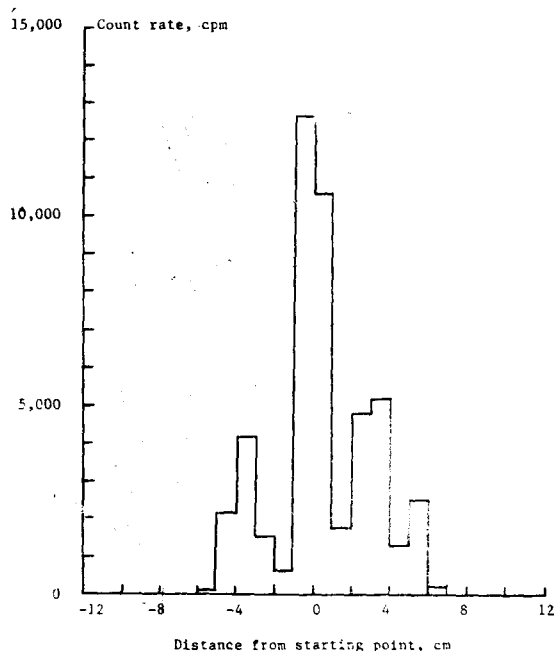


Fig. 3. Paper-electrophoresis Histogram of Ruthenium Chloro-complexes.  
Electrolyte: 0.01M-HCl (pH=2.0)

assumed to be  $(\text{RuCl}(\text{H}_2\text{O})_5)^{2+}$ . The species at +4cm position is probably cis-and trans- $(\text{RuCl}_2(\text{H}_2\text{O})_4)^{1+}$ . The species at -1cm position which remains almost at starting point is assumed to be  $(\text{RuCl}_3(\text{H}_2\text{O})_3)^0$  or  $(\text{RuCl}_4(\text{H}_2\text{O})_2)^{1-}$ . The species at -4cm position is probably  $(\text{RuCl}_6)^{3-}$ . The similar results of paper-electrophoresis with ruthenium chlorocomplexes under 0.1 M-HClO<sub>4</sub> (pH=0.85) and 0.1 M-HCl (pH=1.1) are presented:

Electrolyte	Migration Species	distance
0.1 M-HClO <sub>4</sub>	+8cm	$(\text{RuCl}(\text{H}_2\text{O})_5)^{2+}$
	+5cm	cis-and trans- $(\text{RuCl}_2(\text{H}_2\text{O})_4)^{1+}$
	-1 to +1cm	$(\text{RuCl}_3(\text{H}_2\text{O})_3)^0$ or $(\text{RuCl}_4(\text{H}_2\text{O})_2)^{1-}$
	-5cm	$(\text{RuCl}_6)^{3-}$
0.1 M-HCl	+11cm	$(\text{RuCl}(\text{H}_2\text{O})_5)^{2+}$
	+6cm	cis-and trans $(\text{RuCl}_2(\text{H}_2\text{O})_4)^{1+}$
	-1cm	$(\text{RuCl}_3(\text{H}_2\text{O})_3)^0$ or $(\text{RuCl}_4(\text{H}_2\text{O})_2)^{1-}$
	-5cm	$(\text{RuCl}_6)^{3-}$

### 3.4. Retention

Table 2 shows the retention values of (Ru

Table 2. Retention Values of  $(\text{RuCl}_6)^{3-}$  on Various pH

pH	Electrolyte	Retention, (%)
0.85	0.1M-HClO <sub>4</sub>	17.8
0.9	0.05M-HCl+0.09M-KCl	19.7
1.1	0.1M-HCl	16.4
1.9	$5 \times 10^{-3}$ M-NTA	12.8
2.0	0.01M-HCl	17.3
2.2	0.01M-HClO <sub>4</sub>	18.0
2.6	0.01M-Citric Acid	12.2
6.85	0.01M-KH <sub>2</sub> PO <sub>4</sub> +0.01M-Na <sub>2</sub> HPO <sub>4</sub>	25.4
8.5	0.05M-Borax	64.8
10.0	0.025M-Na <sub>2</sub> CO <sub>3</sub> +0.025M-NaHCO <sub>3</sub>	80.8
11.7	0.01M-Na <sub>3</sub> PO <sub>4</sub>	23.9
12.0	0.01M-NaOH	73.5
13.2	0.1M-NaOH	59.6

$\text{Cl}_6)^{3-}$  in various pH electrolyte solution. Retention is the ratio of ruthenium-106 atoms found in  $(\text{RuCl}_6)^{3-}$  to the total number of the ruthenium-106 atoms. The retention values in 0.1 M- $\text{HClO}_4$ , 0.05 M- $\text{HCl}$ +0.09 M- $\text{KCl}$ , 0.1 M- $\text{HCl}$ , 0.01 M- $\text{HCl}$  and 0.01 M- $\text{HClO}_4$  electrolytes range about 16~20%, because strong acidic solutions make aquo complexes. The low retention value in  $5 \times 10^{-3}$  M-NTA electrolyte is probably due to the complex formation of  $(\text{RuCl}_6)^{3-}$  with nitrirotriactic acid. The highest retention value is found at 0.025 M- $\text{Na}_2\text{CO}_3$ +0.025 M- $\text{NaHCO}_3$  electrolyte solution. Retention values in 0.01 M- $\text{NaOH}$  and 0.1 M- $\text{NaOH}$  electrolytes are about 60~70% due to the addition of  $\text{OH}^-$  ion in strong alkali forming hydroxyl complexes and the decrease of replacement of chloride ion by water.

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