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Studies on the Physico-chemical Behavior of ^{60}Co , ^{106}Ru and ^{144}Ce in Fresh Water

Yuichiro KIMURA,*^{*1} Yoshihiro OGAWA,**^{*1} Masami FUKUI,**^{*2}
Tadashi TSUJIMOTO,**^{*2} Yoshihide HONDA*****^{*1}
and Kosuke KATSURAYAMA*****^{*1}

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Using paper electrophoresis and paper chromatography, changes in the physico-chemical forms of ^{60}Co , ^{106}Ru and ^{144}Ce in fresh water were studied and also compared with those in seawater.

Initial stage of mixing with fresh water, over 90% of ^{60}Co was found in the cationic species, while on the third day, three cationic peaks of electrophoresis were revealed, and electroneutral species including hydrolytic products increased with time.

In the cases of ruthenium complexes (chloro, nitrosyl-nitro, -nitrate, -binuclear complexes), each chemical form had its own characteristic paper electrophoretic behavior in each original solution. After mixing with fresh water, however, hydrolysis and replacement of ligands with H_2O occurred, producing lower-order complexes.

Examination on ^{144}Ce in fresh water showed that over 95% of ^{144}Ce remained at the starting point of paper electrophoresis, suggesting highly adsorptive hydrolytic products might being predominant.

It is noted from the present studies that the tendency of changes in the physico-chemical forms of each radionuclide could be almost similar in both fresh water and aged seawater.

KEY WORDS: physico-chemical forms, ^{60}Co , ^{106}Ru , ^{144}Ce , fresh water, paper electrophoresis, paper chromatography

I INTRODUCTION

In Japan, most of the nuclear facilities such as nuclear power and nuclear fuel reprocessing plants are located or are planned to be located at coastal areas. Therefore, much attention has been paid

to radioactive contamination of the sea and the marine biota. On the other hand, considering release of radionuclides from land repository of radioactive wastes into fresh waters, the behavior and biological concentration of radionuclides in fresh water would be also interested.¹⁻⁴⁾

The chemical composition of open seawater is relatively stable. Therefore, in discussing the biological concentration of radionuclides, the concentration factor for an element in a given species of marine biota varies little among various areas, except for special areas of the sea such as areas near the mouth of a river, areas with a lower or higher salt content and so on.⁵⁾

In the case of fresh water, the pH, chemical composition and rate of water circulation vary greatly among various rivers, lakes and marshes, hence there are large regional differences. Since

* 木村雄一郎, ** 小川喜弘, *** 福井正美, **** 辻本 忠, ***** 本田嘉秀, ***** 桂山幸典

^{*1} Department of Nuclear Reactor Engineering, Faculty of Science and Technology, Kinki University; 3-4-1, Kowakae, Higashiosaka, Osaka 577.

近畿大学理工学部原子 炉 工 学 科; 東大阪市小若江 3-4-1 (〒577)

^{*2} Division of Radiation Control, Research Reactor Institute, Kyoto University; Noda, Kumatori-cho, Sennan-gun, Osaka 590-04.

京都大学原子炉実験所放射線管理部; 大阪府泉南郡熊取町野田 (〒590-04)

the biological concentration factors of radionuclides are greatly affected by these environmental factors as well as physico-chemical forms of the radionuclides, it is necessary to consider them in estimating the impact of radioactive contamination in fresh water environment.

As a series of studies on the physico-chemical behavior of radionuclides in the hydrosphere, the present paper deals with the examination of physico-chemical changes with time of radioactive cobalt, ruthenium and cerium in fresh water using paper electrophoresis and paper chromatography.

II MATERIALS AND METHODS

1. Materials

(1) Fresh water

In this study, river water collected at the Shiga Prefectural Samegai Trout Farm was used. Its limnological characteristics are shown in **Table 1**. Since the content of suspended matters in the river water would vary occasionally, the filtered river water was used to elucidate the changes of physico-chemical forms of the radionuclides in the solution of the river water.

(2) Radionuclides and preparation of test solutions

$^{60}\text{Co}(\text{CoCl}_2)$, $^{106}\text{Ru}(\text{chloro complexes})$ and ^{144}Ce (chloride) purchased from Japan Isotopes Association were used. Nitrosylruthenium nitro-, nitrate- and oxygen bridged binuclear complexes were prepared from ^{106}Ru -chloro complexes in

accordance with the method of FLETCHER *et al.*⁽⁶⁾ Each radionuclide solution adjusted the pH to about 7 was separately added to the river water which had previously been filtered through a Millipore Filter HAWP (pore size of $0.45\ \mu\text{m}$), to obtain the radioactive concentration of about $3.7 \times 10^4\ \text{Bq/ml}$ ($1.0\ \mu\text{Ci/ml}$). The test solutions of pH 7.8 thus prepared were stored in an incubator (about $10 \pm 3^\circ\text{C}$) with or without continuous aeration (about 100 ml/min). An aliquot of these stored solutions was sampled at appropriate time intervals and physico-chemical behavior of the radionuclides was assayed using one-dimensional high-voltage paper electrophoresis or paper chromatography.

2. Experimental equipment and methods

(1) High-voltage paper electrophoresis

For one-dimensional high-voltage paper electrophoresis, an apparatus of the horizontal type with Toyo filter paper strip No. 50 ($2 \times 40\ \text{cm}$) was employed. Approximately $10\ \mu\text{l}$ of the test solution was applied to the central area of the filter paper strip. Electrophoresis was carried out for 20 min using $0.1\ \text{M}\ \text{NaClO}_4$ as an electrolytic solution at a setting of 1,150 V, 20 mA or lower, in a vessel cooled with carbon tetrachloride at $11 \pm 1^\circ\text{C}$. Three filter paper strips were used for each sample in the same conditions.

After electrophoresis, the migration distance of the developed components in the strip was obtained from autoradiograms using medical X-ray films and the radioactivity was measured for each of the fractions divided from the starting point at intervals of 1 cm in the directions of plus and minus sides.

Apparent mobility ($\text{mm} \cdot \text{V}^{-1} \cdot \text{h}^{-1} \cdot \text{cm}$) was calculated using the following equation;

$$u' = \frac{s \cdot b}{t \cdot h}$$

where u' is apparent mobility ($\text{mm} \cdot \text{V}^{-1} \cdot \text{h}^{-1} \cdot \text{cm}$), s is the distance of migration (cm), t is the time of electrophoresis (hour) and h is the voltage of electrophoresis (volt).

(2) Paper chromatography

Each complex of nitrosylruthenium was tested with paper chromatography in accordance with the method of WAIN *et al.*⁽⁷⁾ Toyo filter paper strip No 5A ($1 \times 15\ \text{cm}$) was used. The test solution (about $5\ \mu\text{l}$) was applied to the lower 2 cm area of the filter paper strip.

Table 1 Limnological characteristics of the fresh water.

Tested item	Mean value
Temperature	$11 \pm 1^\circ\text{C}$
pH	7.8
Alkalinity	30.3 ppm
Na	2.6 ppm
K	0.2 ppm
Ca	25 ppm
Cl^-	9.6 ppm
Total dissolved solids	114.7 ppm
Residue after ignition (inorganic)	79.9 ppm
Dissolved organic matter (loss on ashing)	34.8 ppm
Total suspended matter	1.8 ppm
Electrical conductivity	241 $\mu\text{mho/cm}$

Methylisopropyl ketone (MIPK), equilibrated with 3 N nitric acid, was used as a developer. Development was carried out for about 20 min, using the ascending technique at room temperature (about 15°C). Three filter paper strips were also used for each sample in the same conditions.

Immediately after development the filter paper strip was dried and subsequently subjected to autoradiography. After division at intervals of 1 cm, the radioactivity was determined, and the rate of flow (Rf) was calculated using the following equation;

$$Rf = \frac{\text{distance between the starting point and center of spot}}{\text{distance between the starting point and the front of solvent}}$$

All of the radioactivities of samples were measured using a low background counter within counting error of 5%.

III RESULTS

1. High-voltage paper electrophoresis^{8,9)}

(1) Changes in the electrophoretic behavior of ^{60}Co due to aging

Figure 1 shows the changes in the electrophoretic behavior of ^{60}Co in the original dilute HCl solution and in fresh water. The axis of the abscissas indicates apparent mobility from the starting point, and the axis of the ordinates indicates the percentage of radioactivity detected from each fraction compared with the total radioactivity applied to the filter paper.

In the original dilute HCl solution, over 95% of ^{60}Co was found in the form of cationic species which showed a relatively clear distribution, and only several percent remained at the starting point. One hour after mixing with fresh water, over 90% of ^{60}Co was found in the form of cationic species, but the zone of electrophoresis was wider than that manifested by the original dilute

HCl solution, in addition, a small amount of anionic species was found. On the third day, cationic species formed three peaks of different mobilities, and the percentage of electroneutral species remaining at the starting point increased. These electroneutral species tended to increase with time, attaining about 50% on the 59th day.

(2) Changes in the electrophoretic behavior of ^{106}Ru -chloro complexes due to aging

Electrophoretic data for ^{106}Ru -chloro complexes are shown in Fig. 2. In the original dilute HCl solution, anionic species occupied about 70% and showed a relatively clear distribution. The electroneutral species was about 20%, while cationic species was about 6%. One hour after mixing with fresh water, the percentage of anionic species was slight, while electroneutral species was predominant. On the third day, however, the percentage of anionic species became to increase. Anionic species found in fresh water showed a wider zone of electrophoresis compared with that manifested by anionic species in the original dilute HCl solution.

(3) Changes in the electrophoretic behavior of ^{106}Ru -nitrosyl complexes in different chemical forms due to aging

Figure 2 and Table 2 show changes in the electrophoretic behavior of each complex (nitro-, nitrate- and binuclear-) of nitrosylruthenium (RuNO) in fresh water stored under a condition of continuous aeration (air flow rate: about 100 ml/min). Plate 1 shows the autoradiograms for RuNO -complexes.

Electrophoretic patterns indicate that about 90% of the nitro complexes in the original dilute sodium nitrite solution was anionic species, which formed a relatively clear zone of electrophoresis at the mobilities over $5 \text{ mm} \cdot \text{V}^{-1} \cdot \text{h}^{-1} \cdot \text{cm}$. One hour after mixing with fresh water, a highly

Fig. 1 Electrophoretic patterns of ^{60}Co in fresh water medium (static condition).

Fig. 2 Electrophoretic patterns of ^{106}Ru complexes in fresh water medium.

similar electrophoretic pattern was obtained; on the third and subsequent days, however, nitro complexes in fresh water showed a decrease in fractions with the mobilities over $5 \text{ mm}\cdot\text{V}^{-1}\cdot\text{h}^{-1}\cdot\text{cm}$ and an increase in the less mobile anionic species. Nitrato complexes in the original dilute nitric acid solution consisted of electroneutral species of about 77%; anionic and cationic species of about 9% and 14%, respectively. Also in fresh water, most nitrato complexes were found in the form of electroneutral species; cationic species tended to decrease with time, accompanied with an increase in anionic species. The mobility of anionic and cationic species in fresh

water was less than that in the original solutions.

In the examination for binuclear complexes, cationic species contained in the original solution showed a decrease, one hour after mixing with fresh water, accompanied with an increase in electroneutral and cationic species. After that, electroneutral species decrease with time, accompanied with an increase in anionic species. The increase in anionic species was chiefly due to the fractions with the mobilities less than $3 \text{ mm}\cdot\text{V}^{-1}\cdot\text{h}^{-1}\cdot\text{cm}$.

Figure 3 summarizes the changes in the percentage of anionic, cationic and electroneutral species of nitrosylruthenium complexes in fresh

Table 2 Fractions of different forms of radionuclides in fresh water (paper electrophoretic separation).

Time	RI	Form		
		Charged		Electroneutral (Remaining at starting zone)
		Cationic	Anionic	
0 h (original)	^{60}Co	0.96	0.00	0.04
	^{106}Ru -nitro	0.02	0.91	0.07
	^{106}Ru -nitrato	0.14	0.09	0.77
	^{106}Ru -binuclear	0.69	0.24	0.17
	^{106}Ru -chloro	0.06	0.72	0.22
	^{144}Ce	0.46	0.01	0.53
1 h	^{60}Co	0.96	0.02	0.02
	^{106}Ru -nitro	0.04	0.88	0.08
	^{106}Ru -nitrato	0.04	0.13	0.83
	^{106}Ru -binuclear	0.08	0.50	0.42
	^{106}Ru -chloro	0.08	0.18	0.74
	^{144}Ce	0.00	0.01	0.99
3 days	^{60}Co	0.63	0.12	0.25
	^{106}Ru -nitro	0.03	0.91	0.06
	^{106}Ru -nitrato	0.02	0.12	0.86
	^{106}Ru -binuclear	0.05	0.60	0.35
	^{106}Ru -chloro	0.02	0.11	0.87
	^{144}Ce	0.00	0.02	0.98
25–59 days	^{60}Co	0.52	0.00	0.48
	^{106}Ru -nitro	0.04	0.88	0.08
	^{106}Ru -nitrato	0.03	0.22	0.75
	^{106}Ru -binuclear	0.06	0.73	0.21
	^{106}Ru -chloro	0.03	0.33	0.64
	^{144}Ce	0.04	0.02	0.94

water. As seen in this figure, nitro complexes in fresh water were chiefly found in the form of anionic species. The figure also shows that in the case of binuclear complexes, anionic species tended to increase after long-term aging, but that in nitrate complexes, electroneutral species were predominant, although anionic species were also found.

(4) Changes in the electrophoretic behavior of ^{144}Ce due to aging

Figure 4 shows electrophoretic features of ^{144}Ce . In the original dilute HCl solution, over 45% of ^{144}Ce was found in the form of cationic species that migrated slightly toward the cathode, while about 50% remained at the starting point. In

fresh water, most of the ^{144}Ce remained at the starting point until 59th day, and also a small number of anionic and cationic species, which formed a diffused zone of electrophoresis, became to be noticed with time.

2. Paper chromatography⁹⁾

(1) Changes in the paper chromatographic behavior of ^{106}Ru -nitrosyl complexes in different chemical forms due to aging

Figure 5 and Table 3 show the results of paper chromatography carried out to investigate changes in the physico-chemical forms of nitro, nitrate and binuclear complexes of nitrosylruthenium ($^{106}\text{RuNO}$) in fresh water.

In the case of nitrosyl-nitro complexes, the

Plate 1 Autoradiograms of paper electrophoretic patterns of RuNO complexes in fresh water.

fractions corresponding to the dinitro complex ($R_f \geq 0.8$), which had a share of about 41% in the original solution, showed a gradual decrease in fresh water, and the fractions corresponding to the mononitro complex and uncomplexed species ($R_f \leq 0.2$) were increased.

However, the fractions of trinitro complex and higher-order nitro complexes ($R_f: 0.2-0.8$) changed little, even after mixing with fresh water.

In the case of nitrosyl-nitrato complexes, the mononitrato complex and uncomplexed RuNO^{3+} ($R_f \leq 0.2$) occupied about 94% in the original

Fig. 3 Effect of aging on the distribution of ^{106}Ru -NO-complexes in fresh water medium.

solution, while the percentage of higher-order nitrato complexes (di-, tri-, tetra- and pentanitrato complexes) with a R_f over 0.2, was as small as about 6%. These higher-order nitrato complexes rapidly decreased in fresh water. On the first and subsequent days after mixing with fresh water, nearly all of them were found in fractions with a R_f below 0.2.

In the case of nitrosyl binuclear complexes, fractions with a R_f below 0.2, which correspond to mononitrato complex, mononitro complex and uncomplexed species, were about 80% in the original solution. They rapidly increased after mixing with fresh water, reaching over 90% one hour later. On the other hand, fractions with a R_f of 0.2–1.0, which correspond to dinitrato, dinitro and higher-order nitrato or nitro complexes, showed a decrease. On the third and subsequent

Fig. 4 Electrophoretic patterns of ^{144}Ce in fresh water medium (static condition).

Fig. 5 Distribution of ^{106}Ru complexes species in fresh water medium (chromatographic separation in MIPK).

Table 3 Effect of aging on the distribution of RuNO complexes in fresh water (paper chromatographic separation in MIPK equilibrated with 3 N-HNO₃).

Time of aging	RuNO-nitro			RuNO-nitrato		RuNO-binuclear	
	% Ru with R_f			% Ru with R_f		% Ru with R_f	
	R_f 0~0.2	0.2~0.8	0.8~1.0	R_f 0~0.2	0.2~1.0	R_f 0~0.2	0.2~1.0
0 h (original)	16.7	42.5	40.8	93.7	6.3	80.2	19.8
1 h	19.2	40.6	49.2	96.5	3.5	89.8	10.2
3 days	26.3	44.9	28.8	99.9	0.1	92.3	7.7
25 days	31.2	48.4	20.4	99.5	0.5	94.8	5.2

days after mixing with fresh water, no major change was noted in the percentages of these fractions (R_f : 0.2–1.0).

IV DISCUSSION

1. Characteristics of river water used in the experiments

As can be seen in Table 1, the water quality and also the concentrations of major components such as Na, K, Ca, Cl and so on, are in ordinary ranges reported on river waters in Japan.¹⁰⁾ As one of means for speciation of trace radionuclides in sea water, the authors carried out electro-

dialysis with ion-exchange membranes.¹¹⁾ Because of low ion contents in fresh water, however, it was difficult to apply electrodialysis to the river water. Therefore, in the present study, the authors used paper electrophoresis and paper chromatography to study the physico-chemical forms of radionuclides in fresh water.

2. State of ^{60}Co

From the results of paper electrophoresis, it is suggested that ^{60}Co would be hydrolyzed with the lapse of time in fresh water at pH 7.8. The hydrolysis of Co^{2+} at pH 7.8 would be described as follows;

$$\begin{aligned}\text{Co}^{2+} + \text{H}_2\text{O} &\rightleftharpoons \text{Co}(\text{OH})^+ + \text{H}^+, \\ K_{\text{OH}} &= [\text{Co}(\text{OH})^+][\text{H}^+]/[\text{Co}^{2+}], \\ \log([\text{Co}(\text{OH})^+]/[\text{Co}^{2+}]) \\ &= \log K_{\text{OH}} - \log[\text{H}^+] = -2.16 < 0,\end{aligned}$$

as

$$\log K_{1,\text{OH}} = -9.96^{12)}$$

therefore,

$$[\text{Co}(\text{OH})^+] < [\text{Co}^{2+}],$$

and also

$$\begin{aligned}\log([\text{Co}(\text{OH})_2]/[\text{Co}(\text{OH})^+]) \\ = \log K_{2,\text{OH}} + \log[\text{OH}^-].\end{aligned}$$

The concentration of hydroxy ion is calculated to be

$$\log[\text{OH}^-] = -\log[\text{H}^+] - 14,$$

because of $[\text{H}^+][\text{OH}^-] = 10^{-14}$ at 20°C , at pH 7.8,

$$\begin{aligned}\log([\text{Co}(\text{OH})_2]/[\text{Co}(\text{OH})^+]) \\ = \log K_{2,\text{OH}} + \log[\text{OH}^-] = -16.16,\end{aligned}$$

as assumed to be

$$\log K_{2,\text{OH}} \approx \log K_{1,\text{OH}},^{12)}$$

therefore,

$$[\text{Co}^{2+}] > [\text{Co}(\text{OH})^+] > [\text{Co}(\text{OH})_2]^0.$$

On the other hand, there will be some anions such as Cl^- , SO_4^{2-} and so on in river water,¹¹⁾ although only the concentration of Cl^- was determined. Taking into account of the stability constants of complex formations of Co^{2+} with above mentioned anions ($\log K_1: \text{OH}^- > \text{SO}_4^{2-} > \text{Cl}^-$)¹²⁾ and ordinary concentration ranges of such anions in Japanese river waters,¹⁰⁾ inorganic species of Co in the river water of pH 7.8 would be Co^{2+} , $\text{Co}(\text{OH})^+$, CoCl^+ , $\text{Co}(\text{OH})_2^0$, CoSO_4^0 and so on.

3. State of ^{106}Ru

MARAZOVIĆ *et al.*,^{13,14)} KEČKEŠ *et al.*¹⁵⁾ and ISHIKAWA *et al.*¹⁶⁻¹⁸⁾ studied the state of radioactive ruthenium in seawater using electrodialysis with ion-exchange membranes, two-dimensional electrical chromatography or high-voltage paper electrophoresis. These studies revealed that radioactive ruthenium gives various physico-chemical forms (anionic, cationic, electroneutral and particulate, as well as those not adsorptive onto filter paper, those slightly adsorptive onto filter paper, and so on) depending on the difference in original chemical forms of ruthenium prevailing in a stock solution before mixing with seawater.

Paper electrophoresis, which allows quick and easy separation, is generally a useful method for the analysis of ruthenium complexes consisted of numerous anionic, cationic and electroneutral species. Studying with this technique, the orig-

inal solution of chloro complexes was found to involve anionic species (about 70%), electro-neutral species which remained at the starting point (about 20%) and cationic species (about 10%). Immediately and one day after mixing with fresh water, the percentage of anionic species was smaller while that of electroneutral species was larger. On the third day, the anionic species became to increase. However, all of the anionic species found in fresh water showed a wider electrophoretic zone compared that in seawater.¹¹⁾ These changes suggest that the ligand Cl^- of the ruthenium complexes is replaced with H_2O (so-called "aquo"-change). The ligand replacement is generally expressed by the following formula:

One hour after mixing with fresh water, *i.e.*, at the stage of aquo-change, anionic species, $[\text{Ru}(\text{H}_2\text{O})\text{Cl}_5]^{2-}$ or $[\text{Ru}(\text{H}_2\text{O})_2\text{Cl}_4]^-$, showed a marked decrease, while an electroneutral species, $[\text{Ru}(\text{H}_2\text{O})_3\text{Cl}_3]^0$, showed a sharp increase. On the third day, the electroneutral species again peaked. After that, the electroneutral species gradually decreased, accompanied with an increase in anionic species. As seen in Fig. 2, a wide electrophoretic zone was noted in fresh water with time. This seems to be attributable to the following equilibrium, that is,

$$[\text{electroneutral}] \xrightleftharpoons[k_2]{k_1} [\text{anionic}] \xrightleftharpoons[k_2]{k_2} [\text{polymeric}],$$

$$k_1 \gg k_2.$$

In the paper electrophoresis, the original solution of each of the nitro, nitrate and binuclear complexes of nitrosyl-ruthenium had its own characteristics. In the case of nitrosyl-nitro complexes, anionic species were predominant (91%). In the case of nitrate complexes, neutral species remaining at the starting point accounted for about 77%, while anionic and cationic species each accounted for about 10%. In the case of binuclear complexes, cationic, anionic and electroneutral species were 63%, 22% and 15%, respectively.

Comparison of the results in fresh water with those obtained for the original solution of ruthenium complexes revealed that the data for nitro complexes were almost similar between them, while somewhat different in the case of the other ruthenium complexes (Table 2).

This finding indicates that the electrophoretic

behavior for a certain chemical form can vary with the duration of aging or the difference in the conditions of storage of the solution, as has been pointed out by KISO¹⁹⁾ and ISHIKAWA *et al.*²⁰⁾

Table 2 shows a comparison of paper electrophoretic behavior of ruthenium complexes and ^{60}Co and ^{144}Ce in fresh water aged for about one or two months. As seen in the **Table 2**, most nitrosyl complexes were anionic. In the case of nitrate complexes, electroneutral form was noted, and anionic and cationic species were also present. In the case of binuclear complexes, anionic species were dominant in fresh water. ISHIYAMA *et al.*²¹⁾ suggested the possible chemical changes in nitro-nitrosylruthenium binuclear complexes (bridged by oxygen) in a neutral aqueous solution containing sodium nitrate, that is,

as the Ru assumed to be hexa-valent.

This indicates that anionic species are formed by the decomposition of binuclear complexes.

In the present study, the authors also studied physico-chemical changes of nitro, nitrate and binuclear complexes (prepared by the method of FLETCHER *et al.*⁶⁾) using paper chromatography. The separated chemical species of RuNO complexes were identified according to the *Rf* values reported by WAIN *et al.*⁷⁾ This study revealed that in the case of nitro complexes, the percentage of the dinitro complex $[\text{RuNO}(\text{NO}_2)_2(\text{H}_2\text{O})_2\text{OH}]^0$ with a *Rf* over 0.8 gradually decreased in fresh water from about 41 % seen in the original solution. This decrease in the dinitro complex was accompanied with an increase in mononitro and uncomplexed species with a *Rf* below 0.2. These results suggest that the dinitro complex, which was formerly said to be relatively stable in aqueous solutions, is gradually decomposed in fresh water.

BHAGAT *et al.*²²⁾ summarized the chemical behavior of nitro complexes in neutral aqueous solutions as follows:

This indicates that replacement of the ligand NO_2^- and hydrolysis occur.

The dinitrate and higher-order nitrate complexes contained in the original solution decreased in fresh water. On the third and subsequent days, mononitrate and uncomplexed species with a *Rf* below 0.2 accounted for more than 97%, possibly due to replacement of the ligand NO_3^- with the ligand OH^- or H_2O .

In the case of binuclear complexes in fresh water, mononitro, mononitrate and uncomplexed species, *i.e.*, fractions with a *Rf* below 0.2, were increased with time from 80% in the original solution to over 90% on the third and subsequent days. These results suggest that higher-order nitrate complexes and nitrate binuclear complexes are decomposed in fresh water to yield lower-order complexes or uncomplexed species.

From the results above mentioned, it is presumed that each kind of the complexes was hydrolyzed partially to yield negatively charged complexes (probably hydroxy and aquo complexes), accompanied with the formation of electrically neutral nitrosylruthenium hydroxide, $([\text{RuNO}(\text{OH})_3])^0$, and was presumably polymerized to form multinuclear complexes.

4. State of ^{144}Ce

According to HIRANO,²³⁾ trivalent cerium begins to be hydrolyzed at a pH of about 6, while tetravalent cerium begins to be hydrolyzed at a pH of about 3. At higher pH levels, hydrolysis will proceed further as a matter of course. In addition, cerium is well-known to be adsorbed on suspension solids or deposits in water, that is, to take the form of adsorbed particles.²³⁾

Studying the behavior of ^{144}Ce in fresh water using paper electrophoresis, cationic species, which migrated slightly toward to the cathode, were found at about 45% in the original dilute HCl solution, and about 50% of ^{144}Ce remained at the starting point. After mixing with fresh water, over 95% of ^{144}Ce remained at the starting point.

This finding indicates that cerium is hydrolyzed in the fresh water at pH 7.8 and also highly adsorptive products are probably adsorbed on the filter paper, and that the hydrolyzed species of cerium in fresh water have a smaller electric charge density.

Finally, the results obtained from the present studies indicate that in the fresh water of pH 7.8 used here, the radionuclides such as radioactive cobalt, ruthenium and cerium were significantly

hydrolyzed together with dissociation of the bound ligands, although the possible formation of various complexes with various dissolved ligands is not ruled out.

These results would also suggest that the tendency of the physico-chemical forms of each radionuclide eventually became similar in slightly alkaline natural waters, in both fresh water and seawater,¹¹⁾ after much time.

V CONCLUSION

Using paper electrophoresis and paper chromatography, changes in the physico-chemical forms of ⁶⁰Co, ¹⁰⁶Ru and ¹⁴⁴Ce in the environmental hydrosphere particularly in river water were studied and also compared with those in seawater.¹¹⁾

Immediately (one hour) and one day after mixing with fresh water, ⁶⁰Co gave a wider electrophoretic zone than that recorded in the original solution; over 90% of ⁶⁰Co was found in the form of cationic species. On the third day, the electrophoretic zone became to manifest three peaks, and the electroneutral species remaining at the starting point increased. These electroneutral species increased with time, accounting for about 50% on the 59th day. The electrophoretic pattern for cationic species in fresh water was almost the same as that in seawater reported previously.¹¹⁾

In the case of ruthenium chloro complexes, a marked decrease in anionic species was noted one hour after mixing with fresh water, accompanied with a sharp increase in electroneutral species. After that, electroneutral species gradually decreased, while anionic species became to increase with time, thereby manifesting a wide electrophoretic zone, suggesting formation of polymers with anionic charge.

Paper electrophoretic behavior of nitro, nitrate and binuclear complexes of nitrosylruthenium in fresh water showed that most of the nitro complexes were found to be anionic, while nitrate complexes were found to be electroneutral. Binuclear complexes had a larger percentage of anionic species in fresh water than in seawater.¹¹⁾

Paper chromatogram of the dinitro complex which had about 41% of total nitro complexes in the original solution, showed that the complex decreased gradually with time, accompanied with an increase in the mononitro complex and un-

complexed species.

Higher-order nitrate and binuclear complexes were found to be hydrolyzed in fresh water to yield lower-order complexes or uncomplexed species.

Paper electrophoretic behavior of ¹⁴⁴Ce showed that cationic species which migrated slightly toward the cathode, were found to be about 45% in the original solution, and about 50% of ¹⁴⁴Ce remained at the starting point, while in fresh water over 95% of ¹⁴⁴Ce remained at the starting point including probably highly adsorptive products.

These results indicate that a significant hydrolytic reaction of the radionuclides, involving dissociation of bound ligands occurred in the river water of pH 7.8 used in the present studies.

This is also seen from the tendency of the physico-chemical forms of each radionuclide to be almost similar in both fresh water and seawater¹¹⁾ after much time.

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