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Original Scientific Paper

Electrodialysis of ^{106}Ru, ^{56,57,58}Co and ^{65}Zn in Sea Water Through Ion-Exchange Membranes

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Received April 29, 1966

The procedure for studying the migration of microconstituents during electrodialysis of sea water through ion-exchange membranes is described. On the basis of experiments with ^{106}Ru the possibility of separating various stable physico-chemical forms of ruthenium from sea water is presented.

The separation process was controlled by measuring the radioactivity of sea water during electrodialysis, and the adsorption on ion-exchange membranes in order to establish whether various stable physico-chemical forms of ^{106}Ru exist in sea water and whether they can be successfully separated by this method. For comparison of the results, all experiments were also performed using both ^{56,57,58}Co and ^{65}Zn in sea water.

INTRODUCTION

In preliminary electrophoretic experiments on filter paper strips and two-dimensional electrochromatography we found[1] that ^{106}Ru is present in sea water in several stable physico-chemical forms, which can readily be classified into anionic, cationic, electroneutral, particulate, non adsorbable, and more or less adsorbable species on filter paper. In sea water, ^{56,57,58}Co and ^{65}Zn showed one single well defined cationic species[1].

In the present paper the behaviour of ^{106}Ru, ^{56,57,58}Co and ^{65}Zn is investigated during electrodialysis of sea water through ion-exchange membranes.

EXPERIMENTAL AND RESULTS

Apparatus

The apparatus used for electrodialysis of microconstituents in sea water is shown in Fig. 1. The cell consists of five compartments made of lucite. The inner section of the compartments is round and of the same surface area as the electrodes. In the two external compartments, *i. e.* in the anode and cathode compartment, platinum foil electrodes were placed having 24.5 mm. diameters and surface areas of 4.75 cm^2.

In order to remove the products of electrolysis, the platinum electrodes were continuously washed with sea water, represented by the arrows in Fig. 1.

The cell for electrodialysis was divided by ion-exchange membranes into five characteristic compartments — from left to right (Fig. 1.): the cathode, cationic, middle, anionic and the anode compartment. The membranes were of *Zerolit C-20* and *Zerolit A-20* types, produced by the *United Water Softeners Ltd.* The volume of each compartment was 4.75 cm^3.

A direct current voltage of 8 volts was applied to the electrodes. For the control of possible transition of radioactivity into the anode and cathode compartments, the radioacitivity of the effluent sea water was estimated by means of liquid-flow halogen GM counters connected to ratemeters.

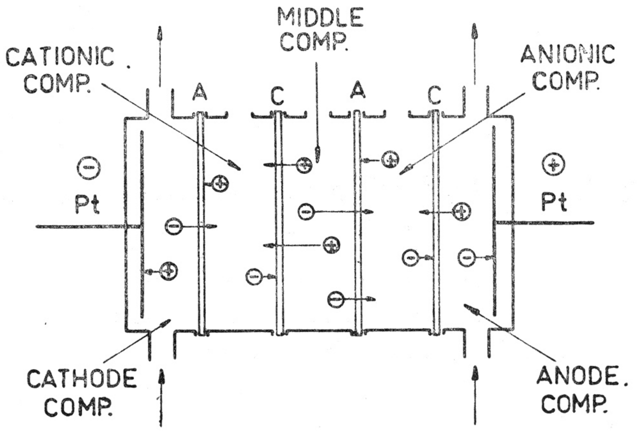

Fig. 1. Schematic diagram of a cell for electrodialysis with ion-exchange membranes.
A — anionic ion-exchange membrane
C — cationic ion-exchange membrane
+ — cation
— — anion
↑ — direction of the electrolyte flow

Electrodialysis of ^{106}*Ru*

4 ml. of sea water were placed into the cationic and anionic compartments of the electrodialysis cell, whereas 4 ml. of sea water contaminated with ^{106}Ru were placed

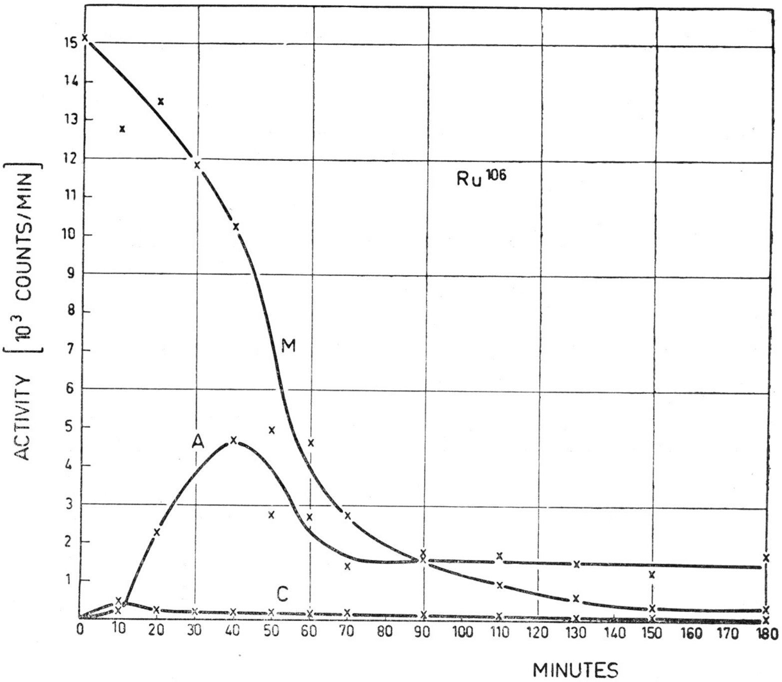

Fig. 2. Graphical representation of the specific radioactivity of ^{106}Ru in the anionic (A), cationic (C) and middle (M) compartment of the cell as a function of the duration of electrodialysis. The specific radioactivity is given in counts/min per 0.1 ml. of solution.

in the middle compartment. The radioruthenium used was a ^{106}Ru nitrosyl-nitrato complex originally dissolved in 8—10 M HNO_3, as supplied by the *Radiochemical Centre,* Amersham. A small drop of this solution was dried under an infra-red lamp to expel the strong acid, and afterwards the sea water was added and the specific radioactivity of the water checked. The salinity of sea water used amounted to 36.67‰. The radioactivity of 0.1 ml. of sea water in the middle compartment was 15,139 counts per minute. The operating voltage of electrodialysis was 8 volts, the current strength decreased during electrodialysis from 150 to 0.6 mA.

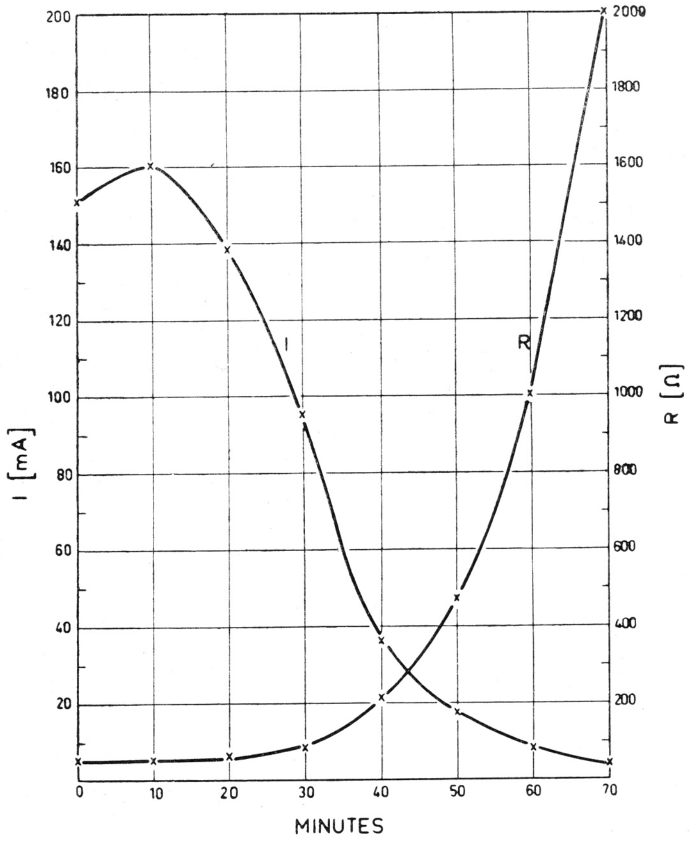

Fig. 3. Graphical representation of the dependence of the current strength and cell electrical resistance on the duration of the electrodialytic process.

Every ten minutes during electrodialysis, samples of sea water (0.1 ml.) were taken from the cationic, anionic and the middle compartment and their radioactivity was measured in counts/min to obtain some insight into the process of electrodialytic migration of the physico-chemical forms of ^{106}Ru. After electrodialysis, the solutions were kept for further use in the investigation of the adsorption on ion-exchange membranes.

A graphical presentation of the electrodialytic process of ruthenium in sea water by radioactivity measurements is shown in Fig. 2.

The progress of the electrodialytic process was followed by measuring the electrical current strength through the cell (Fig. 3.). Table 1. gives the specific conductivity and *pH* of the original sea water and of sea water after electrodialysis in different compartments of the electrodialytic cell.

The results obtained show that the current decreases during the process of electrodialysis owing to an increase in electrical resistance in the middle compartment, *i. e.* desalinization occurred in the middle compartment, whereas accumulation of electrolyte appeared in the cationic and anionic compartment, as seen from the increase of electrical conductivity in these compartments. No significant change in *p*H occurred during the process and this indicates that the critical current density was not exceeded.

TABLE 1.

Some Physico-chemical Data of the Original Sea Water and the Solutions in Compartments After Electrodialysis

	Specific conductivity in Ohms^{-1} cm.^{-1}	*p*H
original sea water	0.0687	8.05
solution from the anionic compartment	0.1020	7.94
solution from the cationic compartment	0.1070	6.50
solution from the middle compartment	0.0019	7.12

The adsorption on ion-exchange membranes was measured to confirm that the physico-chemical forms of ^{106}Ru which migrated into the anionic or cationic compartments during the process were not identical. If this is true, then their adsorption factors on ion-exchange membranes will not be the same. This measurement was done also because, following the electrodialytic process by measuring the radioactivity in the cationic, anionic and middle compartments, it was shown that with time there was a considerable loss of radioactivity in the cell compartments. This loss may be due to adsorption of ruthenium species on the ion-exchange membranes.

Anionic and cationic ion-exchange membranes of surface area 1 cm.^{2} were immersed separately into the initial solution of ^{106}Ru in sea water and into solutions obtained by electrodialysis. These solutions were at least ten days old before they were used in the adsorption experiments. The specific activity of the solutions was previously determined in counts/min per 0.1 ml. Afterwards, the cationic and anionic exchange membranes were immersed into the solutions and the radioactivity of the membranes measured at fixed time intervals. Before counting, the membranes were washed with distilled water. To compare the results obtained from solution of different radioactivities, the adsorption on the membranes was calculated using the adsorption factor:

$$\begin{array}{c}\text{Adsorption}\\ \text{factor}\end{array} = \frac{\text{radioactivity in counts/min per cm.}^2 \text{ of membrane}}{\text{radioactivity in counts/min per 0.1 ml. of solution}}$$

Fig. 4. shows the graphical presentation of the adsorption factor on the anionic and cationic ion-exchange membranes using the initial solution of ^{106}Ru in sea water (*i. e.* prior to electrodialysis) as a function of the duration of adsorption.

As is evident from the figure, adsorption is more intense on the anionic than on the cationic membrane.

The dependence of the adsorption factor of the separated physico-chemical forms of ^{106}Ru in sea water on the duration of adsorption is represented in Fig. 5.

As is seen from the figure, the adsorption of the fraction of ^{106}Ru which migrated into the cationic compartment is strongest on the anionic membrane. A possible explanation is that “cationic” forms in contact with the anionic membrane are not stable and may turn into “anionic” ones, which consequently can be strongly adsorbed on the membrane. This may explain why, during the electrodialytic process, no higher radioactivity in the cationic compartment can be detected. “Cationic” forms of ^{106}Ru arriving into the cationic compartment of the electrodialytic cell are strongly adsorbed on the anionic membrane towards which they are migrating.

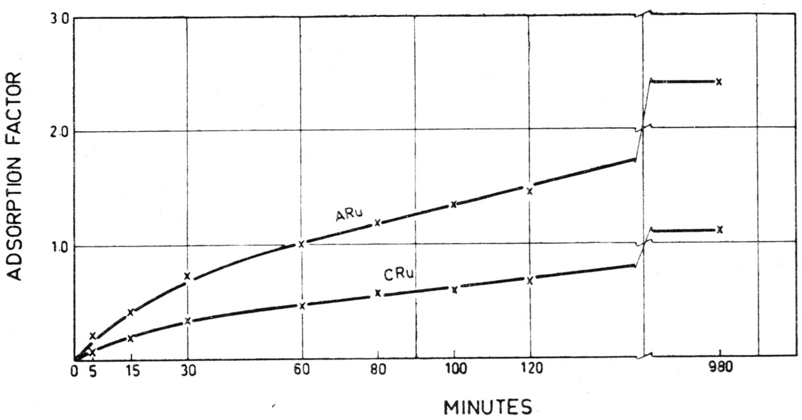

Fig. 4. Graphical representation of the adsorption factors on the anionic and cationic ion-exchange membranes, using the initial solution of ^{106}Ru in sea water, as a function of the duration of adsorption.
A Ru — anionic membrane in the initial solution of ^{106}Ru in sea water
C Ru — cationic membrane in the initial solution of ^{106}Ru in sea water

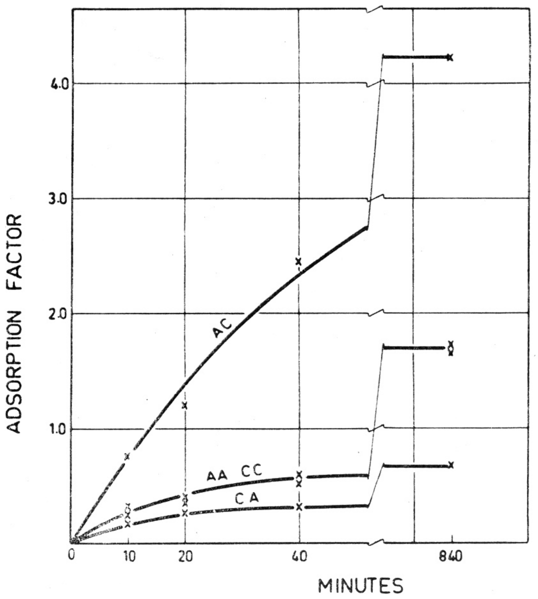

Fig. 5. Graphical representation of the adsorption factors of separated physico-chemical forms of ^{106}Ru in sea water as a function of the duration of adsorption.
A C — anionic membrane in the solution from the cationic compartment
C C — cationic membrane in the solution from the cationic compartment.
A A — anionic membrane in the solution from the anionic compartment
C A — cationic membrane in the solution from the anionic compartment

Electrodialysis of ^{56,57,58}Co

Because of the relatively complicated behaviour of ^{106}Ru in the electrodialytic process of sea water, it was necessary to determine whether and to what degree microconstituents behave identically as macroconstituents during electrodialysis through ion-exchange membranes, while in a relatively concentrated medium such as sea water. For this purpose, a simpler microconstituent was searched for, which was considered to show the characteristics of a single species in sea water. By two- and one- dimensional electrochromatography of $^{56, 57, 58}$Co in sea water, we found[1] that Co as microconstituent behaves as a typical bivalent cation consisting of only one species.

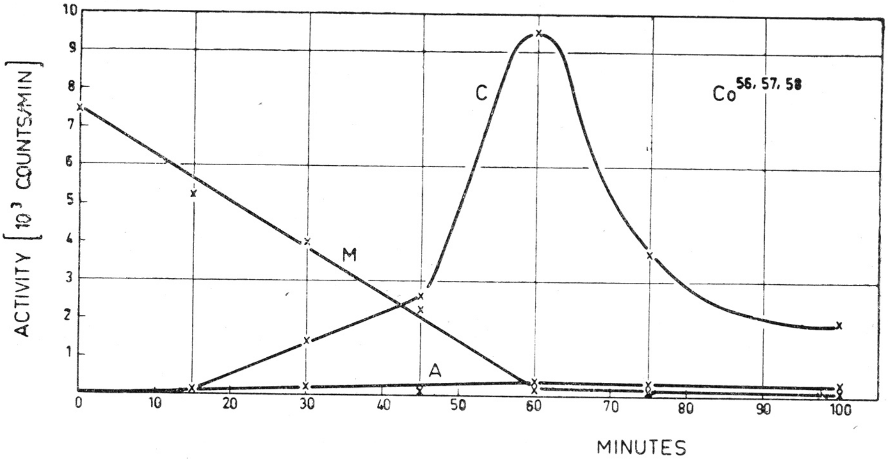

Fig. 6. Graphical representation of the specific radioactivity of ^{56,57,58}Co in the anionic (A), cationic (C) and middle (M) compartment of the cell as a function of the duration of electrodialysis. The specific radioactivity is given in counts/min per 0.1 ml. of solution.

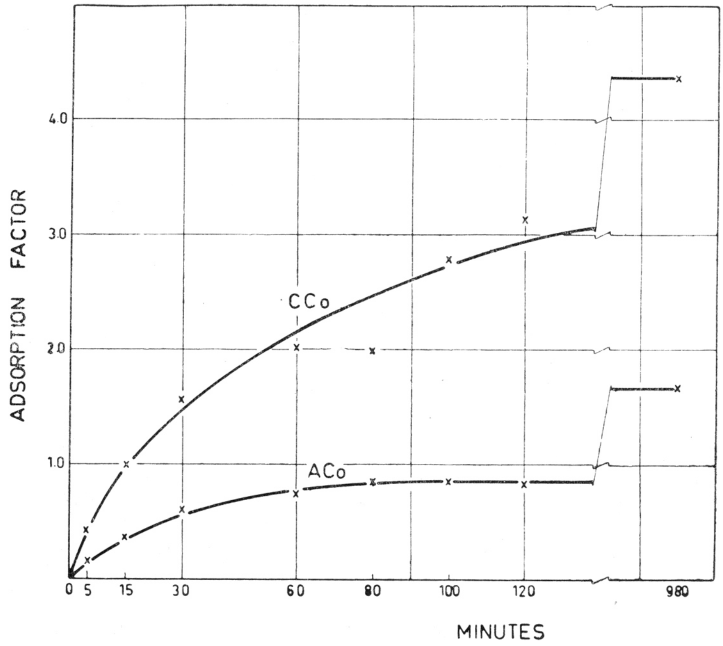

Fig. 7. Graphical representation of the adsorption factors on the anionic and cationic ion-exchange membranes, using initial solution of ^{56,57,58}Co in sea water, as a function of the duration of adsorption.

A Co — anionic membrane in the initial solution of ^{56,57,58}Co in sea water
C CO — cationic membrane in the initial solution of ^{56,57,58}Co in sea water

The experimental conditions for the electrodialytic process of sea water contaminated with $^{56, 57, 58}$Co were identical with those described previously. $^{56, 57, 58}$Co was produced in carrier-free form in the Institute "Ruđer Bošković".

The curve of the specific radioactivity in the anionic, cationic and middle compartment of the electrodialytic cell as a function of the duration of the electrodialytic process is shown in Fig. 6.

The specific radioactivity is expressed as counts/min per 0.1 ml. of solution. As shown in the figure, ^{56,57,58}Co behaves as a cation during the electrodialytic process. Also, the adsorption on the membranes (Fig. 7.) shows that ^{56,57,58}Co, as microconstituent, behaves classically, *i. e.* as a cation, consisting of only one single species.

Electrodialysis of ^{65}Zn

After the experiments with $^{56, 57, 58}$Co, which confirmed that microconstituents behave classically, experiments with ^{65}Zn were carried out. By two- and one-dimensional electrochromatography in sea water it was found that ^{65}Zn, like ^{56,57,58}Co, is present as cation, consisting of a single species[1]. Moreover, the experiment with Zn is interesting because of the amphoteric character of Zn. Thus it is possible to draw

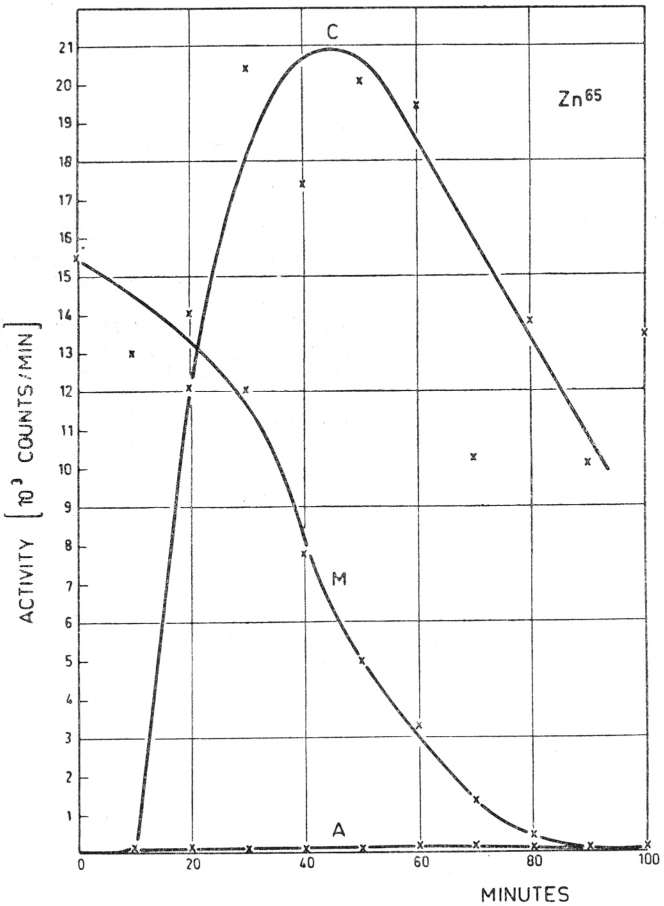

Fig. 8. Graphical representation of the specific radioactivity of ^{65}Zn in the anionic (A), cationic (C) and middle (M) compartment as a function of the duration of electrodialysis. The specific radioactivity is given in counts/min per 0.1 ml. of solution.

a comparison with the adsorption of the cationic forms of ^{106}Ru on the anionic and cationic membranes.

^{65}Zn was produced in carrier-free form in the Institute "Ruđer Bošković". The experimental conditions of the electrodialytic process of sea water contaminated with ^{65}Zn were identical with those described previously in the section of ^{106}Ru.

The curve of the specific radioactivity of ^{65}Zn in the anionic, cationic and middle compartments of the cell as a function of the duration of electrodialysis of sea water is shown in Fig. 8.

As is seen, ^{65}Zn behaves similarly to cobalt as a cation in sea water.

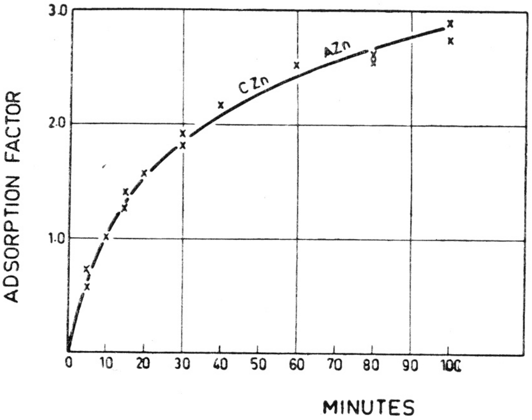

Fig. 9. Graphical representation of the adsorption factor on the anionic and cationic ion-exchange membranes, using initial solution of ^{65}Zn in sea water, as a function of the duration of adsorption.
A Zn — anionic membrane in the initial solution of ^{65}Zn in sea water
C Zn — cationic membrane in the initial solution of ^{65}Zn in sea water

The measurement of the adsorption on the membranes shows that ^{65}Zn in sea water is equally adsorbed on the anionic as on the cationic membranes, which can be deduced from the amphoteric character of Zn (Fig. 9.).

DISCUSSION

From the experiments performed it may be concluded that by the electrodialytic process of sea water using ion-exchange membranes it is possible to separate ^{106}Ru in three compartments: the anionic, electroneutral and cationic, with the specific physico-chemical properties. The separated forms are stable in sea water, even if the solution is left standing for several days at room temperature. This was established by repeated adsorption experiments on ion-exchange membranes. Whilst in contact with an anionic membrane, the "cationic" forms of ^{106}Ru, *i. e.* forms of ^{106}Ru from the cationic compartment of the cell, are not stable. They probably turn into "anionic" forms and, as such, are adsorbed on the membranes. The process of electrodialysis gives the same evidence, for in the cationic compartment, after its initial increase, the radioactivity begins to decrease. This is due to the adsorption of "cationic" forms of ^{106}Ru on the anionic membrane towards which these forms were moving under the influence of the electric field.

Experiments performed simultaneously with ^{56,57,58}Co and ^{65}Zn have shown that ^{56,57,58}Co behaves as a classical cation in the case of electrodialysis as well as membrane adsorption. Co is adsorbed more intensely on the cationic ion-exchange membrane than on the anionic one.

In the electrodialytic process, Zn behaves as a cation, but is equally adsorbed on an anionic as on a cationic exchange mambrane, thus showing its amphoteric properties.

Further, it has been shown that in electrodialysis with ion-exchange membranes, ions in great dilution, *i. e.* as radionuclides of tracer radioactivity and in carrier-free form, also behave as if they were present in common chemical concentrations.

Acknowledgement. This work was supported by the International Atomic Energy Agency contract No. 201/RB and Federal Nuclear Energy Commission of Yugoslavia contract No. 1002/3-1966.

REFERENCE

1. *Annual Report on IAEA Research Contract No.* 201/RI/RB-1965.

IZVOD

Elektrodializa ^{106}Ru, ^{56,57,58}Co i ^{65}Zn u morskoj vodi kroz ionsko-izmjenjivačke membrane

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Opisano je ispitivanje migracije mikrokonstituenata tokom procesa elektrodialize morske vode kroz ionsko-izmjenjivačke membrane. Na osnovi eksperimenata s ^{106}Ru pokazalo se da je moguća separacija različitih stabilnih fizičko-kemijskih formi rutenija u morskoj vodi.

Proces separacije je bio kontroliran mjerenjem radioaktivnosti morske vode tokom elektrodialize i adsorpcijom na ionsko-izmjenjivačkim membranama, da bi se utvrdilo da li postoje različite stabilne fizičko-kemijske forme ^{106}Ru u morskoj vodi i da li se one mogu ovom metodom uspješno odijeliti. Radi komparacije rezultata sva navedena ispitivanja provedena su i s ^{56,57,58}Co i ^{65}Zn u morskoj vodi.

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Primljeno 29. travnja 1966.