TWO-DIMENSIONAL ELECTROCHROMATOGRAPHY OF [106]RUTHENIUM AND SOME OTHER RADIOMICROCONSTITUENTS IN SEA WATER

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INTRODUCTION

Electromigration techniques on a supporting medium seem to be very useful means of investigating the ionic species of an element in water solution if present in several relatively stable physico-chemical forms. The effect of aging of $[Ru(H_2O)Cl_5]^{2-}$ in 0.1 M hydrochloric acid was studied by SHUKLA[1], aging of K_2RuCl_6 in $HClO_4$ and HCl solutions by FORCHERI *et al.*[2], while the behaviour of ruthenium when RuO_4 is reduced by H_2O_2 in perchloric acid and sulphuric acid solutions was investigated by KOCH AND BRUCHERTSEIFER[3]. Separation of the ionic species of [106]Ru from hydrochloric acid solutions in 0.8 M α-oxyisobutyric acid was performed by AITZET-MÜLLER *et al.*[4], while the preparation of a single species from a [106]Ru solution was followed by one-dimensional electrochromatography by LEDERER AND SHUKLA[5].

In the course of biological experiments studying the uptake, loss and accumulation of some radionuclides in marine biota, we realized the importance of studying the physico-chemical forms of the inorganic microconstituents present or introduced into sea water. Evidence about the physico-chemical state of a particular radionuclide which is a microconstituent in sea water should be of great importance in the final interpretation of biological experiments.

For the analysis of this problem, in general, electromigration techniques combined with the use of radioactive tracers have been widely used in this Institute. Electromigration techniques are considered to be a very convenient means of giving the following information about the physico-chemical behaviour of radionuclides introduced as microconstituents into sea water:

(1) The number of stable physico-chemical species of a defined microconstituent present in sea water under variable conditions.

(2) A preliminary characterization of the species present, such as the estimation of the sign of the net electrical charge of electrokinetic units.

(3) Evidence on the adsorbability of the various physico-chemical forms on porous adsorbent media.

The electromigration techniques used were:

(1) Low voltage filter paper strip electrophoresis in a wet chamber[6].

(2) High voltage and strong current electrophoresis or electrochromatography on filter paper strips[7,8].

(3) Two-dimensional electrochromatography on filter paper sheets, and filter paper sheets loaded with cationic and anionic ion-exchange resins[9,10].

(4) Electrodialysis of sea water through ion-exchange membranes. Sea water was previously labelled with radionuclides representing microconstituents or radio-active contaminants which could possibly be introduced by waste disposal[10,11].

In the present paper the techniques 1, 2 and 3 were used.

EXPERIMENTAL AND RESULTS

The apparatus used for two-dimensional electrochromatography[9] and for high voltage electrochromatography[7] has been described earlier.

The experimental data for two-dimensional electrochromatography were as follows: basic electrolyte, 30 vol. % sea water of original salinity $37.56^0/_{00}$ which means that the salinity was actually $11.50^0/_{00}$; free width of filter paper sheets, 30 cm; voltage, 120 and 150 V; current, 40–75 mA; duration of two-dimensional electrochromatography, 2 or 3.5 h; time of exposure to X-ray film, 12 to 16 h.

The experimental data for high voltage electrochromatography on filter paper strips were: basic electrolyte, 100 % sea water of original salinity $37.56^0/_{00}$; filter paper, Munktel 20/100; free length of filter paper strips, 66 cm; free width of filter paper strips, 1.5 cm; voltage, 1200 V; current, 24–28 mA per one strip; duration of high voltage electrochromatography, 33 min.; temperature, 18–20°.

The sea water was filtered prior to use by forcing it by means of a peristaltic pump, first through the Seitz asbestos bacteriological filter and then through a Millipore HA filter.

Preliminary investigation of the characteristic behaviour of some important radionuclides in sea water[10] was done by two-dimensional electrochromatography using sea water as a background electrolyte. Sheets of Munktel No. 20/100 filter paper were used and the results were developed by radioautography on an X-ray film.

[51]Cr in the chromate form showed no adsorption on filter paper and gave, as expected, only one well-defined anionic species. [22]Na, [54]Mn, [56,57,58]Co and ^{90}Sr were not adsorbed on filter paper but each element showed a definite single cationic species. [65]Zn and ^{90}Y showed a considerable chromatographic effect but as in the case of the preceding radioisotopes only one cationic species of each element could be detected. It was found that all the above mentioned radioisotopes exist in sea water in one single soluble species, and no insoluble or particulate form could be detected.

[51]Cr, ^{59}Fe, [95]Nb, [95]Zr, [144]Ce, [147]Pm and [181]Hf were strongly adsorbed on filter paper at the starting point, presumably because of the formation of strongly adsorbable or insoluble hydrolytic species, or particle formation.

[106]Ruthenium exposed to two-dimensional electrochromatography in sea water showed a relatively large number of well-defined species which can be readily classified into anionic, cationic, electroneutral, particulate, non-adsorbable and more or less adsorbable species on filter paper. Because of the complexity of the results the electrochromatography of [106]Ru was examined here more extensively.

Two 1 mC samples of [106]Ru from the Radiochemical Centre, Amersham were used, one of them was a sample in chloride form, dissolved in 8 M hydrochloric acid, the other was a sample in nitrate form dissolved in about 8 M nitric acid. The acid was removed from both samples by evaporation to dryness under an infra-red lamp. The residue was dissolved in 0.01 M HCl in the case of chloride form, and in 0.01 M

HNO$_3$ in the case of nitrate form. Another portion of dry residue of both ruthenium samples was dissolved in sea water. Prior to use the solutions were left standing at least four days. This aging of the solutions was found to be satisfactory, the samples aged between 4 and 90 days without aeration showed the same positions and number of spots. Two-dimensional and one-dimensional electrochromatography of the above four [106]Ru samples was carried out on Munktel No. 20/100 filter paper (Fig. 1), Schleicher and Schüll cation-exchange paper with 5 % Dowex 50 (Fig. 2) and on Schleicher and Schüll anion-exchange paper with 5 % Dowex 2-X8 (Fig. 3). Some characteristics of the ion-exchange resins used are given in Table I.

TABLE I

SOME CHARACTERISTICS OF ION-EXCHANGE RESINS USED

Resin	Matrix	Group	Capacity mequiv./g	pH range
Dowex 50	Polystyrene	—SO$_3^-$	4.9–5.2	0–14
Dowex 2-X8	Polystyrene	—N(alkylol)(alkyl)$_2^+$	3.0	0–12

From the experiments illustrated in Figs. 1, 2 and 3 it is evident that the behaviour of [106]Ru in sea water depends on the form of the original sample (chloride or nitrate form). By comparison of the radioautograms marked (a) and (b) with the radioautograms marked (c) and (d) it is obvious that [106]Ru in the nitrate form is composed mostly of anionic and electroneutral species. The presence of cationic species is most pronounced in ruthenium samples which were originally present in the chloride form. The electrokinetic behaviour of anionic species in chloride form are markedly different from those in nitrate form.

Comparison of radioautogram (a) with (b) and of the radioautogram (c) with (d) shows that some differences exist depending on whether the ruthenium samples are equilibrated in 0.01 M acid or in sea water of pH about 8. It is somewhat surprising, but may be of particular interest, that the cationic fractions of the chloride form in sea water were not adsorbed on Dowex 50 cation-exchange paper, see Fig. 2 (a) and (b). On the other hand, on Dowex 2-X8 anion-exchange paper, as expected, all anionic species were adsorbed at the starting point, the cationic species not being affected by the anion-exchange resin (Fig. 3). Essentially the same results were obtained by high voltage electrophoresis in sea water of 37.56°/$_{00}$ salinity, but the interpretation of these one-dimensional electrochromatograms was not found to be so simple, because of the lack of the two-dimensional resolution of the chromatographic and electrochromatographic effects. By raising the concentration of sea water only the electrochromatographic mobilities of species were proportionally diminished.

Another portion of [106]Ru was converted to RuO$_4$ by the distillation method[12, 13]. [106]Ru nitrosyl-nitrato complexes in 8 M HNO$_3$ were evaporated to dryness, dissolved in 0.5 M H$_2$SO$_4$, transferred to a distillation flask, and the distillation of RuO$_4$ was started after addition of a few milligrams of nonradioactive Ru in sulphate solution, Ag$_2$SO$_4$ as a catalyst and (NH$_4$)$_2$S$_2$O$_8$ as an oxidant. The distillation flask was heated to about 80°. The RuO$_4$ vapors were carried away by means of a moderate stream of
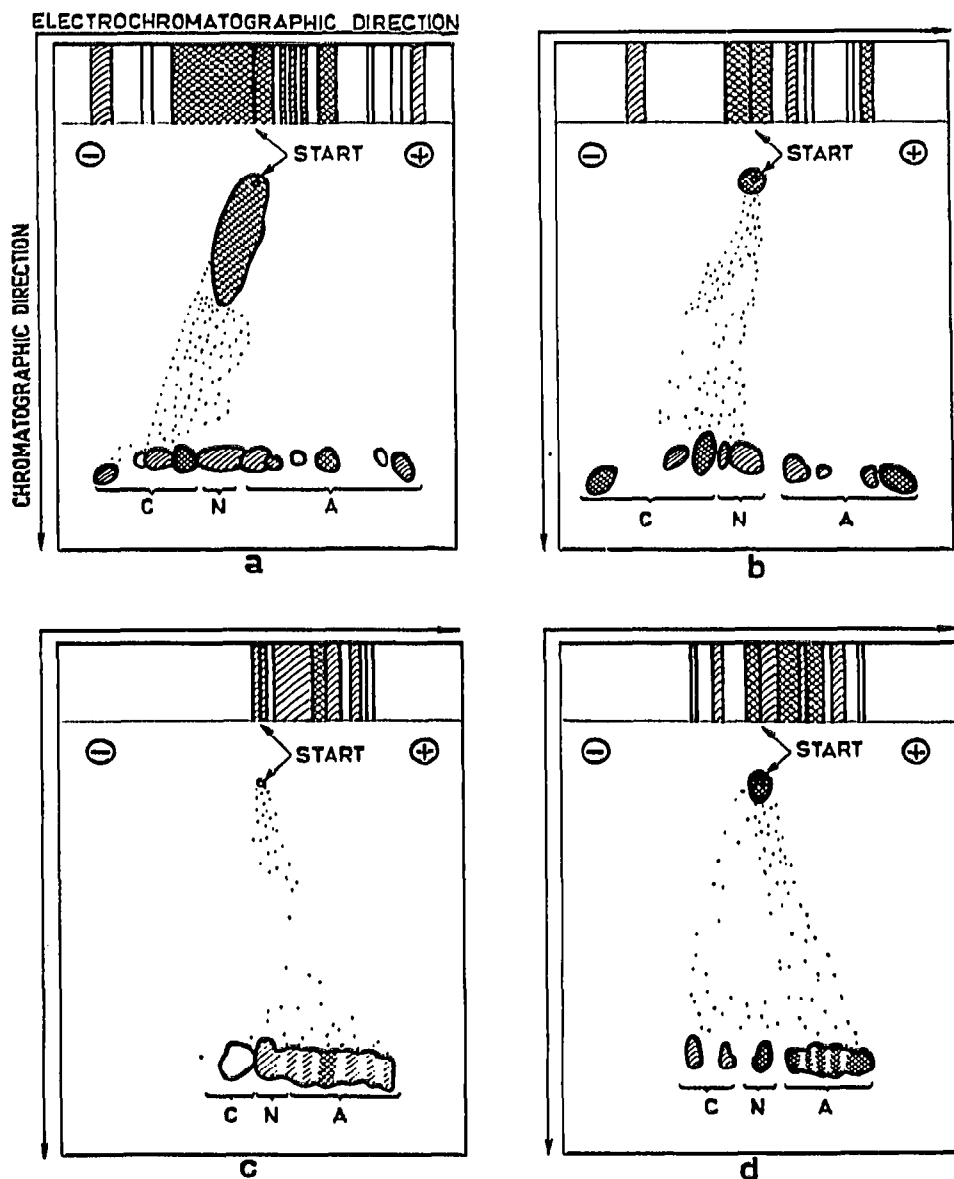
Fig. 1. Radioautograms of two-dimensional electrochromatograms and the corresponding one-dimensional electrochromatograms (upper edges) of ^{103}Ru in sea water on filter paper Munktel 20/100. Basic electrolyte, 30 % sea water of original salinity 37.56⁰/₀₀ (actual salinity 11.50⁰/₀₀); voltage 150 V; current 40–75 mA; duration 3.5 h. Shading of the spots on radioautograms represents the relative intensity of ruthenium species. (a) ^{106}Ru chloride form dissolved in 0.01 M HCl; (b) ^{106}Ru chloride form dissolved in sea water; (c) ^{106}Ru nitrate form dissolved in 0.01 M HNO$_3$; (d) ^{106}Ru nitrate form dissolved in sea water. A = Anionic forms; C = cationic forms; and N = electroneutral forms.
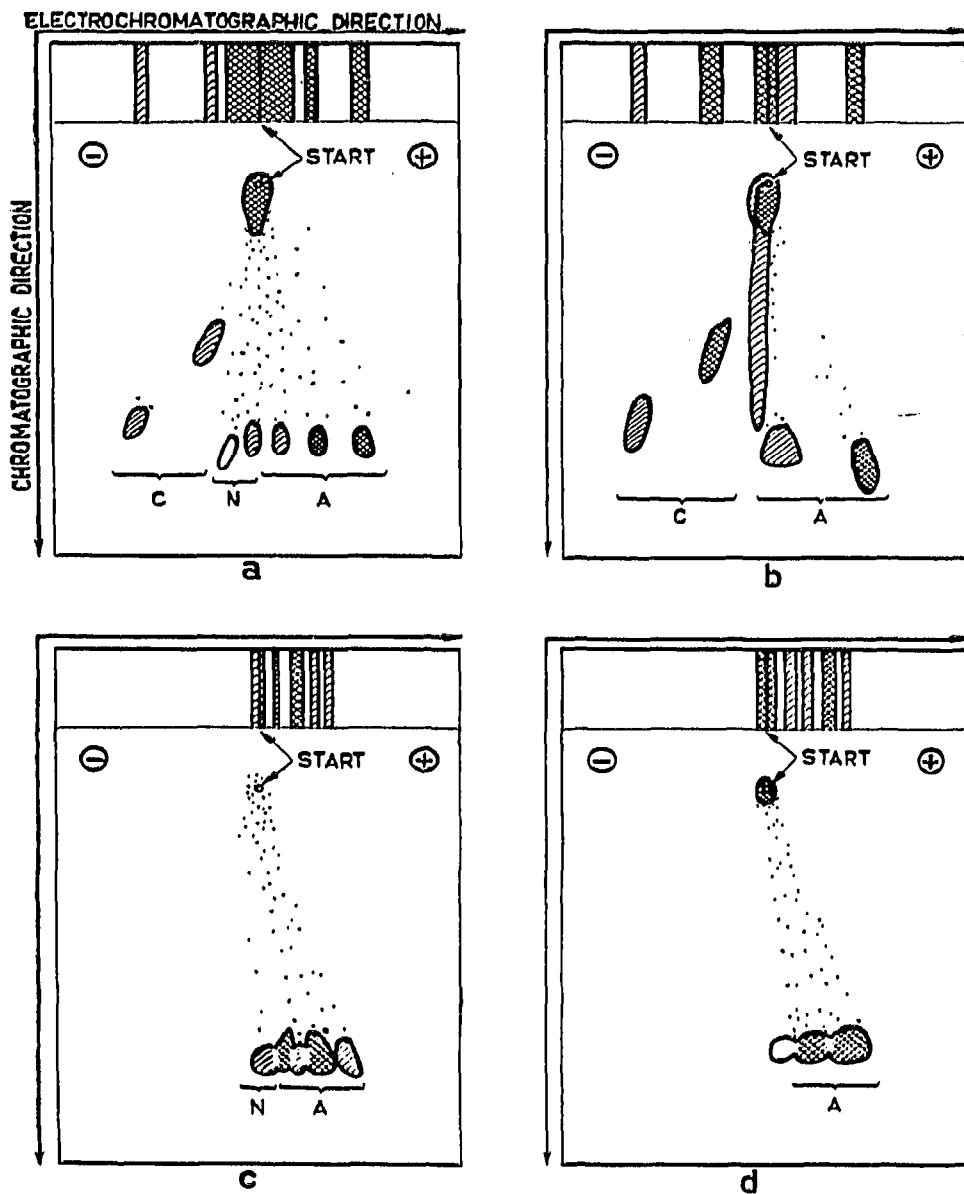
Fig. 2. Radioautograms of two-dimensional electrochromatograms and the corresponding one-dimensional electrochromatograms (upper edges) of ^{106}Ru in sea water on Schleicher and Schüll cation ion-exchange paper with 5% Dowex 50. Basic electrolyte, 30% sea water of original salinity $37.5^0/_{00}$ (actual salinity $11.50^0/_{00}$); voltage 120 V; current 40–50 mA; duration 2 h. Shading of the spots on radioautograms represents the relative intensity of ruthenium species. (a) ^{106}Ru chloride form dissolved in 0.01 M HCl; (b) ^{106}Ru chloride form dissolved in sea water; (c) ^{106}Ru nitrate form dissolved in 0.01 M HNO$_3$; (d) ^{106}Ru nitrate form dissolved in sea water. A = Anionic forms; C = cationic forms; and N = electroneutral forms.
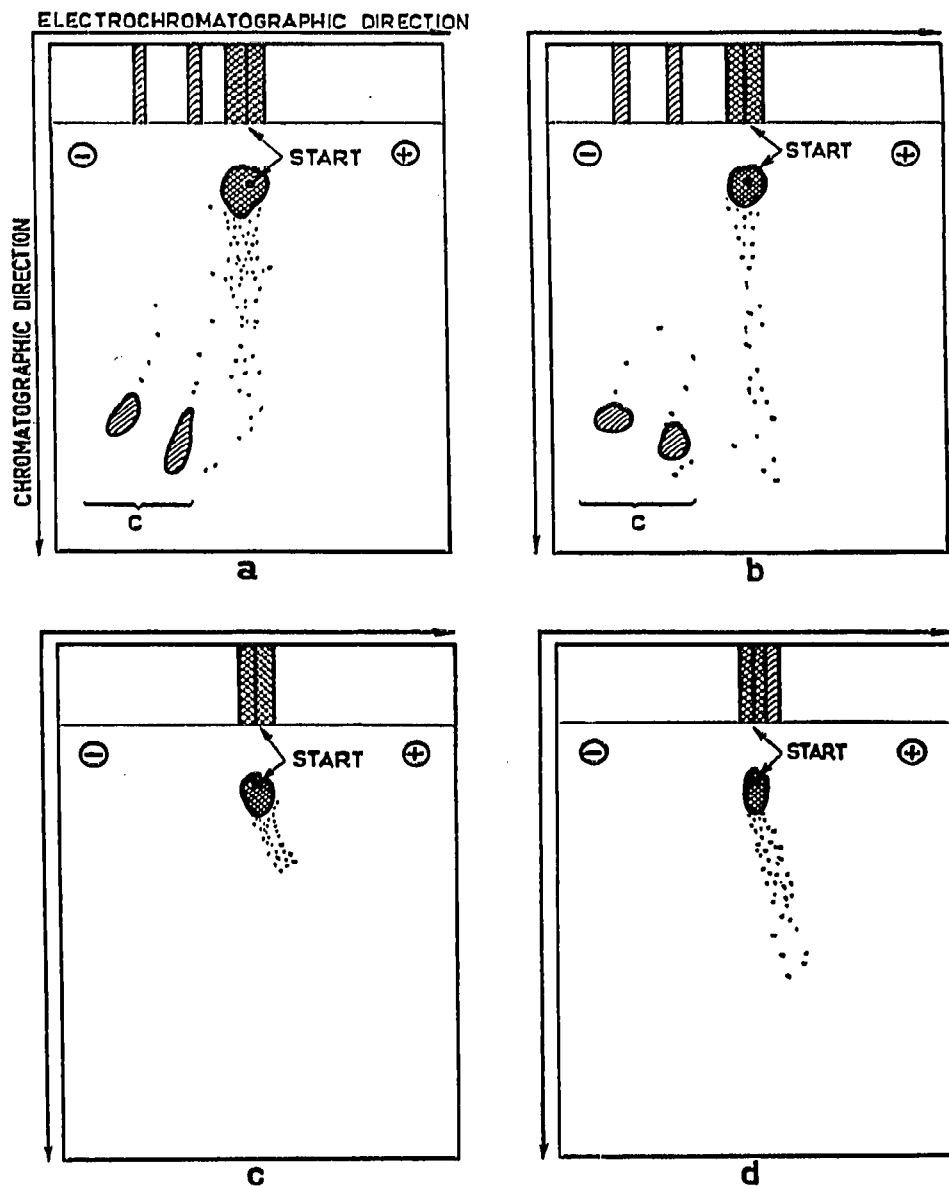
Fig. 3. Radioautograms of two-dimensional electrochromatograms and the corresponding one-dimensional electrochromatograms (upper edges) of [106]Ru in sea water on Schleicher and Schüll anion ion-exchange paper with Dowex 2-X8. Basic electrolyte, 30 % sea water of original salinity 37.56$^0/_{00}$ (actual salinity 11.50$^0/_{00}$); voltage 120 V; current 25–35 mA; duration 2 h. Shading of the spots on radioautograms represents the relative intensity of ruthenium species. (a) [106]Ru chloride form dissolved in 0.01 M HCl; (b) [106]Ru chloride form dissolved in sea water; (c) [106]Ru nitrate form dissolved in 0.01 M HNO$_3$; (d) [106]Ru nitrate form dissolved in sea water. C = Cationic forms.

TABLE II

RESULTS OF TWO-DIMENSIONAL ELECTROCHROMATOGRAPHY IN 30% SEA WATER OF ORIGINAL SALINITY $37.56^0/_{00}$ (*i.e.* S $= 11.50^0/_{00}$) AND OF HIGH VOLTAGE ELECTROCHROMATOGRAPHY IN 100% SEA WATER (S $= 37.56^0/_{00}$) OF SOLUTIONS DERIVED FROM RADIOACTIVE RuO_4

The two-dimensional electrochromatography was carried out, if not further commented, 60 days after distillation and 35 days after the treatment of $1\ M$ HCl and $1\ M\ HNO_3$ solutions.

[106]Ru solution		Results of two-dimensional electro-chromatography and high voltage electrochromatography	Comments
RuO_4 absorbed in sea water		Starting point: strong spot Anionic fractions: none Cationic fractions: none	Till 6 days after distillation two very weak cationic spots were also recorded
RuO_4 absorbed in distilled water		Starting point: strong spot Anionic: none Cationic: none	The same results 5 to 90 days after distillation
RuO_4 absorbed in $1\ M$ HCl, evaporated to dryness	redissolved in 0.01 M HCl	Starting point: strong spot Anionic: one very weak spot Cationic: some trailing	The same results 25 to 90 days after distillation
RuO_4 absorbed in $1\ M$ HCl, evaporated to dryness	redissolved in sea water	Starting point: strong spot Anionic: one very weak spot Cationic: none	The same results 25 to 90 days after distillation
RuO_4 absorbed in $1\ M\ HNO_3$, evaporated to dryness	redissolved in 0.01 $M\ HNO_3$	Starting point: strong spot Anionic: some trailing Cationic: some trailing	The same results 25 to 90 days after distillation
RuO_4 absorbed in $1\ M\ HNO_3$, evaporated to dryness	redissolved in sea water	Starting point: strong spot Anionic: some trailing Cationic: some trailing	The same results 25 to 90 days after distillation

air, and the distillation was completed in half an hour. The addition of nonradio-active Ru as a carrier was necessary. The distilled radioactive RuO_4 was absorbed separately in ice cooled $1 M$ HCl, $1 M$ HNO_3, distilled water and sea water. The HCl and HNO_3 solutions are fairly stable at room temperature between 6 and 90 days giving, on high voltage electrochromatography in $1 M$ HCl and $1 M$ HNO_3, respec-tively, several well-defined cationic and anionic spots with a relatively weak spot at the starting point. This indicates that stable ruthenium chloro complexes and nitrosyl-nitrato complexes were found. In the case of the HCl solutions three anionic spots and one cationic spot were found, whereas in the HNO_3 solutions two cationic spots, one very weak and the other very strong, were evident on radioautography. It should be noted here that these radioautograms do not correspond to the radioautograms obtained with the Amersham samples which show a much greater variety of species (10 and sometimes more). Distilled water and sea water solutions of RuO_4 are un-stable yielding a precipitate of insoluble oxides in particulate form. The $1 M$ HCl and HNO_3 solutions were evaporated to dryness 25 days after distillation, the resi-dues dissolved in 0.01 M HCl, 0.01 M HNO_3 or sea water. In such a way we obtained solutions which, with respect to treatment, correspond to solutions prepared from the already described Amersham [106]Ru samples, the difference being that in this case the ruthenium was in the well-defined RuO_4 form at the moment of absorption in $1 M$ HCl and $1 M$ HNO_3.

The solutions derived from radioactive RuO_4 were subjected to two-dimensional electrochromatography and to high voltage electrochromatography. The results depicted from radioautograms are given in Table II.

By spectrophotometric measurements of RuO_4 solutions in distilled water and in filtered sea water we found that RuO_4 is stable in such solutions in the form of the tetroxide at low temperatures and in the dark. When kept at room temperatures and exposed to daylight for between two and six days after distillation, it turned to insoluble oxides. In contact with filter paper, RuO_4 decomposed immediately into insoluble lower valency oxides, which on two-dimensional electrochromatography or electrophoresis on filter paper gave a strong adsorbable spot at the starting point and no mobile fractions. In the case of solutions of RuO_4 in sea water, until 6 days after distillation we found two very weak cationic spots indicating the presence of two intermediate cationic complex species between RuO_4 and lower valency oxides.

RuO_4 absorbed in $1 M$ HCl and $1 M$ HNO_3 gives several stable lower valency complexes as indicated by high voltage electrochromatography performed in $1 M$ concentrations of the corresponding acid. After the treatment, *i.e.* after the evapor-ation of excess acid and dissolving in 0.01 M acid, these solutions give, by high voltage electrochromatography in $1 M$ acid, the same results as the original acid solutions. On the other hand, as seen from Table II, after high voltage electro-chromatography in 100 % sea water (S = 37.56^0/$_{00}$) and two-dimensional electro-chromatography in 30 % sea water (S = 11.50^0/$_{00}$), the treated acid solutions generally only give one firmly adsorbed spot at the starting point. The results obtained indicate that it was not possible to prepare the physico-chemical species of ruthenium corres-ponding to the samples commercially available from Amersham by the distillation of ruthenium and absorption of RuO_4 in $1 M$ HCl or $1 M$ HNO_3 acid solutions.

DISCUSSION

The relatively large number of stable species of ^{106}Ru present in sea water, and other aqueous solutions, may be explained by the special ability of ruthenium to exist in a variety of oxidation states between plus one and plus eight, and to its property of readily forming stable complexes, especially nitrosyl-, nitro-, nitrato-, chloro-, hydroxo- and aquo[14-19] complexes.

From the two-dimensional electrochromatogram it is not immediately predictable which of the possible forms should be attributed to a certain spot of the two-dimensional electrochromatogram of ^{106}Ru, and this problem requires further investigation.

The present experimental results may give some evidence about the possible fate and behaviour of ^{106}Ru, which may be discharged into sea water and oceans as a result of waste disposal from nuclear fuel reprocessing plants, or which may contaminate sea water as a result of fall-out. The waste from reprocessing is usually in strong acid solutions, whereas the fall-out may contain, to a certain degree, ruthenium in the form of tetroxide.

Originally acid solutions of ruthenium can affect the presence of the variety of stable, soluble physico-chemical species of ruthenium in sea water, whereas ruthenium tetroxide introduced into sea water is quickly decomposed giving lower valency insoluble oxides in particulate form. The life of soluble forms of ruthenium in sea water depends mostly on the amount and quality of suspended particulate matter present in sea water.

It would be of interest to separate on a preparative scale the soluble species of ruthenium stable in sea water to enable one to study and compare the rate of uptake and loss of different physico-chemical species or groups of species of ruthenium by marine biota.

Experiments are in progress along these lines and results will be published elsewhere.

ACKNOWLEDGEMENTS

SUMMARY

Two-dimensional electrochromatography, on filter paper sheets and filter paper sheets loaded with ion-exchange resins, of ^{106}Ru and some other microconstituents using sea water as a background electrolyte are described. The results are developed by radioautography on an X-ray film.

Some of the microconstituents, ^{51}Cr as chromate, ^{22}Na, ^{54}Mn, ^{56,57,58}Co, ^{90}Sr, ^{65}Zn and ^{90}Y, showed no, or a slight, adsorption on filter paper and each of them gave one single mobile fraction. The others were strongly adsorbed on filter paper at the

starting point, as ^{51}Cr, ^{59}Fe, ^{95}Nb, ^{95}Zr, ^{144}Ce, ^{147}Pm and ^{181}Hf, presumably because of the formation of strongly adsorbable hydrolytic species or particle formation.

Samples of ^{106}Ru from Amersham in chloride form (original in 8 M HCl), and in nitrate form (original in 8 M HNO$_3$), were used after a preliminary treatment.

Experimental evidence shows that, in sea water, ^{106}Ru behaves very differently, depending on the form of the original sample (chloride or nitrate form).

The two-dimensional electrochromatography of ^{106}Ru in sea water showed a relatively large number of well-defined species which could be readily classified into anionic, cationic, electroneutral, particulate, non-adsorbable and more or less adsorbable species on filter paper. Although anionic fractions, as expected, were strongly adsorbed on anion ion-exchange paper (Dowex 2-X8), cationic fractions of ruthenium in chloride form were not adsorbed on cation ion-exchange filter paper (Dowex 50).

The same experiments were also performed starting from RuO$_4$, which was obtained by a distillation method. The fate of RuO$_4$ and soluble species resulting from decomposition of the tetroxide in HCl and HNO$_3$ solutions and in sea water, was studied.

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