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SEPARATION OF THE RECOIL PRODUCTS OF INORGANIC PHOSPHORUS OXYACIDS BY CROSS ELECTROPHORESIS

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An attempt was made to separate the recoil products of phosphorus oxyacids (salts of hypophosphite, phosphite, orthophosphate and pyrophosphate) by a cross electrophoresis using zinc ions. This electrophoresis was found to have a general applicability to the isolation of a trace amount of a proper compound from a given matrix which forms insoluble complexes.

The chemical effects of the nuclear reaction $^{31}P(n,\gamma)^{32}P$ in inorganic phosphorus compounds have been extensively studied.[1,2] Some discrepancies between the results of various workers seem to be due to a poor chemical separation method as well as different irradiation conditions. In order to improve the resolution of the paper electrophoresis, background buffer solutions of different pH's and/or the buffer solutions containing zinc ions have been used.[3-5] However, when the neutron-irradiated target materials such as pyrophosphate forming insoluble complexes with zinc ions are dissolved in the solution containing zinc ions, the recoil products of the carrier free concentration precipitate along with the target and do not migrate under the electric field. Thus, on discussion on the chemical behavior of hot atoms in the targets in different oxidation states it is an urgent problem to find an electrophoretic method which is applicable to separation of all the phosphorus oxyacids. For this purpose, we applied a cross electrophoresis and obtained successful results.

Target materials of special purity ($NaH_2PO_2\cdot 2H_2O$, $Na_2HPO_3\cdot 5H_2O$, $Na_2HPO_4\cdot 2H_2O$ and $Na_4P_2O_7\cdot 10H_2O$) were purchased from Nakarai Chemical Ltd. The salts (ca. 10mg) of phosphorus oxyacids were sealed in a polyethylene tube and irradiated with thermal neutrons (5×10^{12} n/cm$^2\cdot$ sec) for 60min at reactor temperature in the pneumatic tube of

KUR (Research Reactor of Kyoto Univ.). After having been cooled for a week, each irradiated sample was dissolved in distilled water. The apparatus and procedures except the spot position of the sample were similar to those described in a previous paper.6) Background buffer solutions of different pH values were prepared by mixing 0.1 M nitric acid, 0.1 M sodium hydroxide and 0.1 M sodium acetate. As the migration behavior of carrier free compounds does not show usual one under the lower ionic strength7) ($\leqq 10^{-5}$), the ionic strength was maintained to be 0.1 throughout this experiment. A Whatman 3 MM filter paper (1x60cm) was dipped into the buffer solution and an excess of the solution was removed with another filter paper. An aliquot of the solution containing zinc ions was spotted at the position 10cm from the anodic side and an aliquot of the phosphorus oxyacid solutions at the position 10cm from the cathodic side. After 60min migration at 1500V/45cm at 18 ± 2°C, the activity on the filter paper was located by autoradiography and measured with an autoradioscanner. The identification of recoil products was made by comparing their mobilities and Rf values6) with those of standard compounds.8)

As a side experiment, $^{65}ZnCl_2$ solution was crossed with $H_3{}^{32}PO_4$ solution or pyrophosphate over the pH range of 2 ~ 10 of the background buffer solutions. Further, in order to know the quantitative relationship between zinc ions and phosphorus oxyanions, the cross electrophoresis was carried out at various ratios (1 ~ 10) of zinc ions to orthophosphate or pyrophosphate anions in alkaline regions.

Referring to the results of the side experiments, we analyzed the cross electropherograms of the recoil products. The activities near 10cm is due to the complexes formed with zinc ions and phosphorus oxyanions.

In the case of the irradiated hypophosphite (A), no activity was found near the crossing zone (~ 10cm of the migration distance) as shown in Fig.1. The electropherograms show that the phosphorus oxyacids in higher oxidation state such as orthophosphate and pyrophosphate were little in the recoil products of hypophosphite. When 5μl of the sample solution was crossed with 100μl of the zinc solution, the migrations of all recoil products were retarded by a weak interaction with which the recoil products were not stopped near 10cm. The main recoil products of hypophosphite were phosphite, hypophosphite and hypodiphosphate which was identified from the hydrolysis products.9) In the case of the irradiated phosphite (B), main recoil product was the retention product accompanied with a small amount of orthophosphate. The activity at the starting position seems to be due to originally non-dissociable phosphorus products. The crossing of 20 ~ 50μl of the zinc solution is suitable for

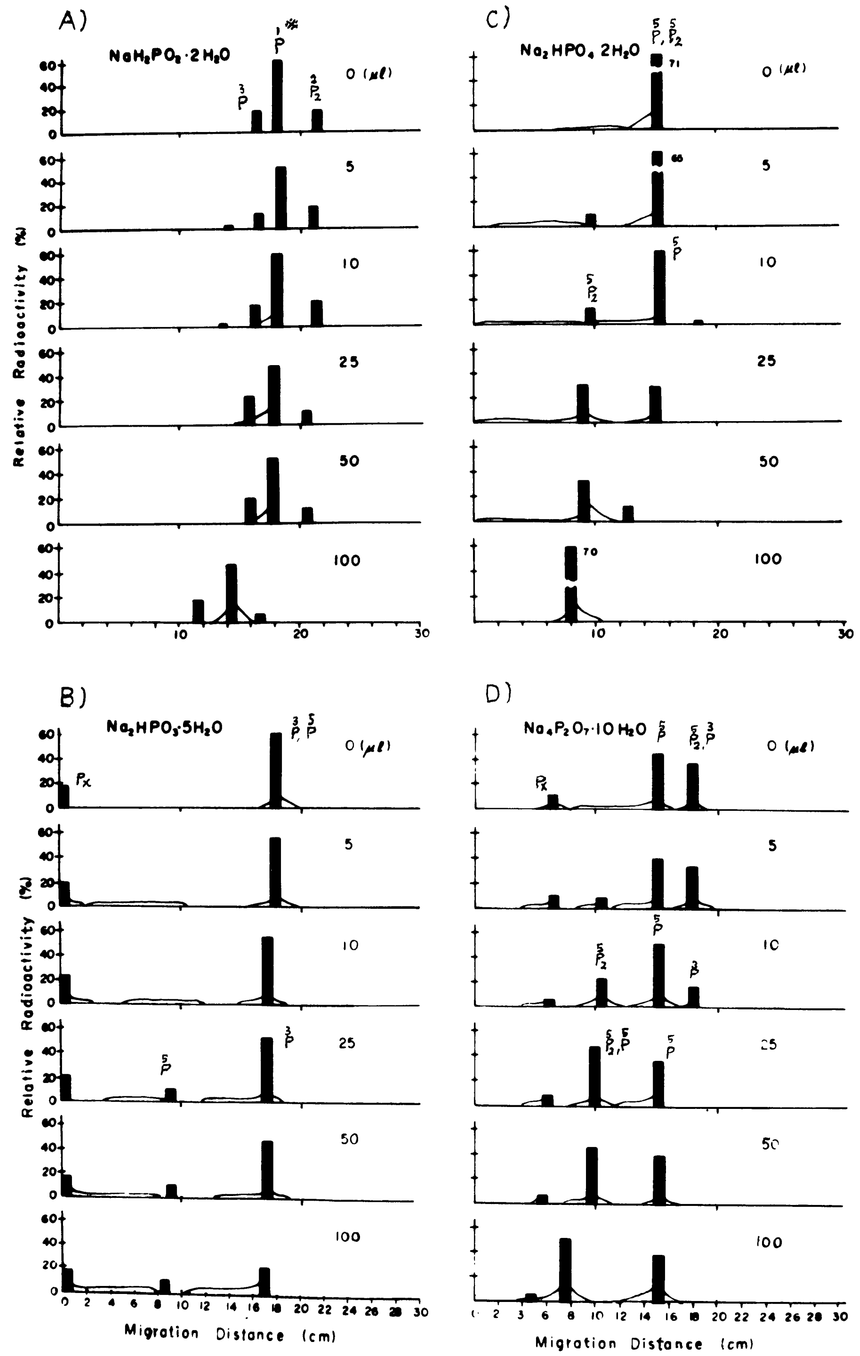

Fig.1. Cross electropherograms of recoil products of phosphorus oxyacids. Figures in the graph show the spot volume of 1/30 M zinc acetate. Chemical formulas show the target materials. ※ Blaser and Worms notations show the main fraction of the peak.

the separation of orthophosphate from the other phosphorus oxyacids in higher oxidation state. Only one big peak was found at 5μl of zinc ions crossing with the irradiated orthophosphate(C). The activity at the crossing zone (~10cm) increased with inceasing amount of zinc ions and finally most activities except tailing were found at the crossing zone. In the case of 5~10μl of zinc ions, the activity found at the crossing zone is mainly due to pyrophosphate. Orthophosphate also was trapped as zinc ions increased. Two main peaks in the electropherograms of pyrophosphate (D) were orthophosphate and pyrophosphate. Pyrophosphate ions were found to have moved farther than orthophosphate because at 25μl of zinc ion solution a larger amount of activity had appeared at the crossing zone ($\sim$10cm) at the sacrifice of the front peak.

Since the neutron irradiation of the salts of phosphorus oxyacids was carried out at the ambient reactor temperature, there was a possibility that some primary recoil products, which were found in the irradiation at dry ice temperature or at liquid nitrogen temperature,[4)] turned into more stable compounds. However, these electropherograms clearly show the tendency that the target in higher oxidation state gave the more amount of recoil products in higher oxidation state than in lower oxidation state.

From these results it is concluded that the yield and kind of recoil products should carefully be estimated on the electrophoretic separation by using metal complex formation reaction because the formation of neutral or non-moving species of phosphorus oxyacids largely depended upon the pH value of the background buffer solution and the concentration and ratio of phosphorus oxyacids to zinc ions. This cross electrophoresis was found to be potentially useful to the isolation of a trace amount of a proper compound from a given matrix which forms insoluble complexes with cations or anions or which is a mixture containing originally non-dissociable compounds.

REFERENCES

1) M. Halmann, Chem. Revs., 64, 689 (1964).

2) L. Lindner and G. Harbottle, "Chemical Effects of Nuclear Transformations" IAEA, Vol.1, p.485, Vienna, 1961.

3) J. Fenger, Risö Report (Denmark), No. 95, (1964).

4) J. Fenger, Radiochim. Acta, 10, 138 (1968).

5) T. Deguchi, K. Ujimoto and S. Ohashi, Bunseki Kagaku, 18, 981 (1969).

6) Y. Kiso, M. Kobayashi, Y. Kitaoka, K. Kawamoto and J. Takada, J. Chromatogr., 36, 215 (1968).

7) P. Benes, V. Urbanova and E. Vidova, Radiochim. Acta. 17, 209 (1972).

8) Y. Kiso, M. Kobayashi, Y. Kitaoka, K. Kawamoto and J. Takada, Bull. Chem. Soc. Japan, 40, 2779 (1967).

9) M. Kobayashi, J. Takada and Y. Kiso, Radiochem. Radioanal. Letters, 9, 67 (1972).

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