

solution) either with 2 *N* nitric acid (spotted as X), or with 2 *N* hydrochloric acid (spotted as Y).

Spots on the startline, designated as Z, were prepared by spotting the solution Y and spraying with sodium hypobromite, and after drying they were sprayed twice with 2 *N* acetic acid.

The samples were spotted on two discs of Whatman No. 3 chromatographic paper. On the first, two samples of X and four samples of Y were spotted. On the second chromatogram there were two samples designated as Z and four samples designated as Y. The system of detection and the nature of detection agents are given in Fig. 1.

One run took about 40 min in the solvent system used, and a complete analysis was finished within 1.5 h (mostly passive working time). After development the chromatograms were dried and cut into six sections, each for detection purposes.

Laboratory of Physiology, Czechoslovak Academy of Sciences, and
Central Research Institute of Food Industry, Prague (Czechoslovakia)

ZDENĚK DEYL
JAN ROSMUS

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Cation-exchange separation of protactinium-233 from irradiated thorium

A knowledge of the analytical separation of protactinium is of technical importance in connection with the chemical processing of irradiated thorium. Several ion-exchange methods have been proposed for separating protactinium from thorium¹⁻⁶. Because of strong hydrolytic and irreversible behavior of protactinium in contact with glass and metal surfaces, most of the ion-exchange systems suffer from an appreciable loss of protactinium during the ion-exchange chromatographic process except for the system involving hydrofluoric acid as a component of eluent. We have been exploring the effective ion-exchange procedures for several elements in thiocyanate-hydrochloric acid media⁷⁻¹⁰. The present paper describes a new ion-exchange chromatographic procedure for separating carrier-free protactinium-233 from neutron-irradiated thorium with a strong acid cation exchanger in thiocyanate-hydrochloric acid solution. Because of the tendency of protactinium to form a stable complex with thiocyanate ions, the cumbersome hydrolytic property of protactinium can almost be excluded so that the rapid separation of protactinium-233 from irradiated thorium was achieved with a shorter column.

Experimental

Dowex 50 W, X-8, of "analytical grade", was used (particle size 100 to 200-mesh). Before use the resin was further purified as described before⁷. Two grams of the

J. Chromatog., 18 (1965) 438-440

dried resin in the hydrogen form was slurried with water and passed into a small ion-exchange column, internal diameter 1 cm, pulled to a tip, and plugged with glass wool at the outlet of the column. The resulting bed was 4 cm long. Eluent was fed on to the top of the column through a 100 ml separatory funnel attached to the inlet of the column.

Protactinium-233 was produced by irradiating approximately 25 mg of thorium nitrate in a TRIGA MARK II reactor of St. Paul's University, Yokosuka, for 6 h at a neutron flux of 5×10^{11} n/cm²/sec. The activity of the protactinium-233 was measured in a standard well-type scintillation counter. Thorium was determined by titration with 0.001 M EDTA solution using Xylenol Orange as indicator.

Procedure

Before use the resin column is treated with a thiocyanate solution (1 M NH₄SCN–0.5 M HCl). The irradiated thorium nitrate is dissolved in 5 ml of the same thiocyanate solution as is used for the column treatment. The sample solution is loaded onto the top of the column and allowed to pass down the column at a flow rate of ~ 0.6 ml per min. Elution of the protactinium-233 is commenced with 1 M NH₄SCN–0.5 M HCl solution, at a flow rate of ~ 0.8 ml per min, when the sample solution almost reaches the top of the column. The protactinium-233 is recovered in the first 100 ml of the effluent. Removal of the thorium is completed by elution with approximately 55 ml of 2 M NH₄SCN–0.5 M HCl solution. The effluent is collected and titrated for thorium with EDTA after diluting with water.

Results and discussion

Protactinium does not adsorb to any great extent from the 1 M NH₄SCN–0.5 M HCl solution, while the thorium shows an equilibrium distribution coefficient of about 150 on a Dowex 50-like cation exchanger, Diaion SK 1, in the same solution⁷. Thus, the difference in the equilibrium distribution coefficients of protactinium and thorium is large enough for a good separation with this cation exchanger. Typical elution profile curves are shown in Fig. 1 for the separation of protactinium-233 and thorium. The elution band which appears with maximum counting rate near 15 ml

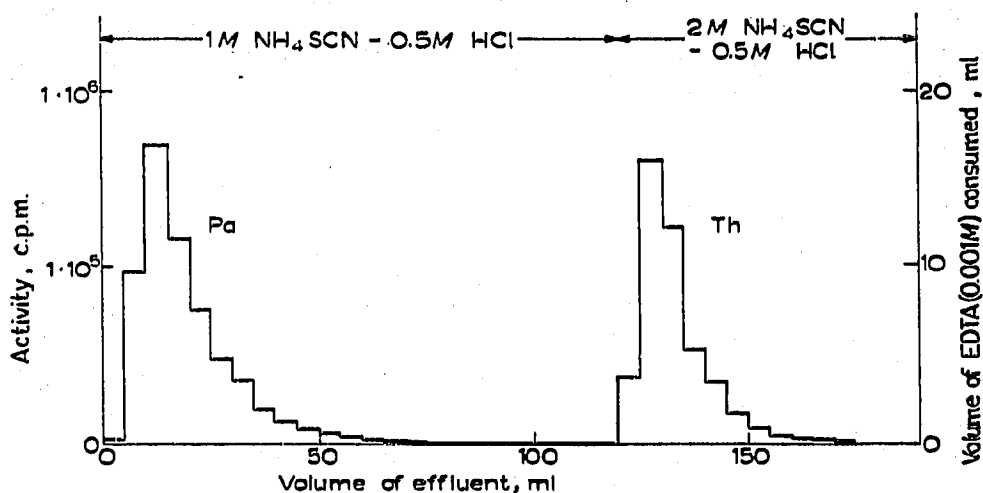


Fig. 1. Separation of carrier-free protactinium-233 from irradiated thorium.

was found by γ -spectrometry to consist of protactinium-233. No other peaks due to foreign activities were found. Recovery of thorium is quantitative. No color reaction of thorium-Xylenol Orange complex was found in the eluted fractions of protactinium. Almost 90% of the protactinium-233 is effectively recovered in the first 50 ml of effluent. Cross contamination of protactinium in the eluted thorium fraction comes to about 1% of the total activity of protactinium concerned. Only 6% of the protactinium-233 was found to remain on the ion-exchange column, mostly on the glass wool used for the plug at the outlet of the column.

The retention of the protactinium is considered to be due to the protactinium fraction which is not thiocyanato-complexed. Even in a protactinium solution in 0.01 M HF-6 M HNO₃, a few per cent of the protactinium was found not to be fluoro-complexed⁴.

The elution behavior of protactinium does not seem to be affected seriously by the flow rate of the eluant. Slowing the flow rate down to a half still produces much the same elution curve as illustrated in Fig. 1. Uranium behaves like protactinium, but is removed much more easily in a sharp band, so that the fissile uranium-233, daughter of protactinium-233 and the desired product of thorium bombardment, can effectively be enriched in the eluted protactinium fraction.

The present method of isolation of protactinium-233 is rapid and gives a reasonably high recovery of carrier-free protactinium-233 without loss of thorium. If desired, the procedure can readily be adapted to handling substantially larger amounts of irradiated thorium. The column can also be operated without attention during the operation step.

*Department of Chemistry, Tokyo Kyoiku University,
Koishikawa, Tokyo (Japan)*

ROKURO KURODA
KOJI ISHIDA

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