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ORNL 330
CHEMISTRY-SEPARATION
PROCESSES FOR URANIUM

CHEMISTRY DIVISION

CHEMISTRY OF PROTACTINIUM

V. SEPARATION OF THORIUM, PROTACTINIUM AND URANIUM WITH ANION EXCHANGE COLUMNS IN HCL SOLUTIONS.

KURT A. KRAUS

GEORGE E. MOORE

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CHEMISTRY OF PROTACTINIUM

V. Separation of Thorium, Protactinium and Uranium with Anion Exchange Columns in HCl Solutions.

Kurt A. Kraus and George E. Moore

Abstract

Using an anion exchange column (with Dowex A-1 resin) thorium, protactinium and uranium have been separated in HCl solutions.

CHEMISTRY OF PROTACTINIUM

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1. Introduction

Since it was found that protactinium in HCl solutions can be adsorbed on and eluted from an anion exchange column prepared with Dowex A-1 resin,(1) it appeared of interest to investigate the applicability of anion exchange techniques to the separation of protactinium from other metal ions, and particularly from thorium and uranium. It was expected that simultaneously some information might be obtained regarding the formation of negatively charged chloride complexes of these elements.

2. Experimental Procedure and Materials

The experiments were carried out with Pa^{233} tracer (β -emitter, $T_{\frac{1}{2}}$ = 27.4 days(2), preparation previously described(1)), U^{233} (alpha emitter,

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(1) K. A. Kraus, G. E. Moore, Report ORNL-329, April 1949.

(2) Information from "Table of Isotopes" by G. T. Seaborg and I. Perlman, Rev. Modern Phys., 20.585 (1948).

$T_{\frac{1}{2}} = 1.6 \times 10^5$ years(2)) and Th^{230} tracer (ionium, alpha emitter, $T_{\frac{1}{2}} = 82{,}000$ years(2)). To increase the thorium concentration, some experiments were also carried out with added thorium (C.P. $ThCl_4 \cdot 8H_2O$).

The resin, adsorption columns, and general techniques were previously described(1). In order to obtain a continuous record of the alpha activity of the eluent, the previously described(3) alpha-solution counter and flow cells were used. In this procedure, open flow cells are placed below a converted Simpson Proportional counter whose counting chamber is separated from the solution by a thin window to retain the counting gas (methane) and to prevent moisture from entering the counting chamber.

In some experiments, supplementary alpha and beta counting of aliquots by the standard plate techniques was carried out to increase the accuracy of the assays.

3. Results

a) Separation of Thorium and Protactinium. It was found that this separation can be carried out to any desired degree, even with every high concentrations of thorium and tracer concentrations of protactinium. Thorium is apparently not appreciably adsorbed by the resin even in practically concentrated HCl, and the columns can generally be operated under breakthrough conditions. A typical separation is illustrated in Fig. 1, where

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(3) K. A. Kraus, G. W. Smith, reported in CNL-37, Quarterly Report of the Chemistry Division, December 1947-February 1948.

the initial adsorption was carried out from 8 M HCl, under which conditions protactinium was quantitatively adsorbed and thorium appeared after the first few column volumes of eluent.*

All thorium could be removed from the column by washing it with 8 M HCl. In view of the extremely high distribution coefficients of protactinium under these conditions, it remained adsorbed at the top of the column, as determined by probing with a collimated GM tube. Thus it appears that for this separation very short adsorption columns can be used, i.e., much shorter than the 15 cm. column used here. Similarly, batch separation using small amounts of resin should be both feasible and rapid.

Practically quantitative recovery of the protactinium, free of thorium, was possible by elution with HCl of lower concentration (1 to 4 M HCl). Using this method separation of tracer protactinium from 0.5 M thorium chloride has been carried out, and there appears to be no reason why protactinium could not be removed from thorium of even higher concentration.

b) Separation of Uranium and Protactinium. This separation is considerably more difficult than that of protactinium and thorium, since uranium (as UO_2^{++}) is adsorbed by the anion exchange resin in a similar manner to protactinium. However, separation can be achieved by selective elution. A typical separation is shown in Fig. 2. For this experiment protactinium and uranium (as well as thorium) were adsorbed from 8 M HCl, and the column developed with 3.80 M HCl (flowrate 0.2 ml cm^{-2} sec^{-1}) after extensive washing with 8 M HCl (to

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* With the small diameter columns used, the volume of connecting tubings and flow cells amounted to several column volumes, making it difficult to determine the volume of eluent needed for the initial break-through of thorium.

remove thorium). It can be seen from Fig. 2 that under these conditions protactinium appears first in the eluent, sufficiently separated from the uranium band to make it appear that with somewhat longer columns the separation would be satisfactory for most purposes.

It may be noticed from Fig. 2 that after ca. 60 column volumes the eluent contained a practically constant amount of Pa^{233} activity. It is probable that this residual amount of activity is due to slow removal of Pa^{233} contamination from the system, rather than slow elution from the resin. However, to resolve this point further experiments are necessary, particularly elutions with lower concentrations of HCl, where it is to be expected that the elution bands are more symmetrical and of smaller half-width.

The strong adsorption of uranyl ions in strong HCl suggests that it can form a negatively charged chloride complex, with charge of at least minus 2. Since the distribution coefficients must be very high, a charge of minus 3 or minus 4 appears probable, which would suggest the formulas $UO_2Cl_5^{-3}$ or $UO_2Cl_6^{-4}$ for the adsorbed complex.

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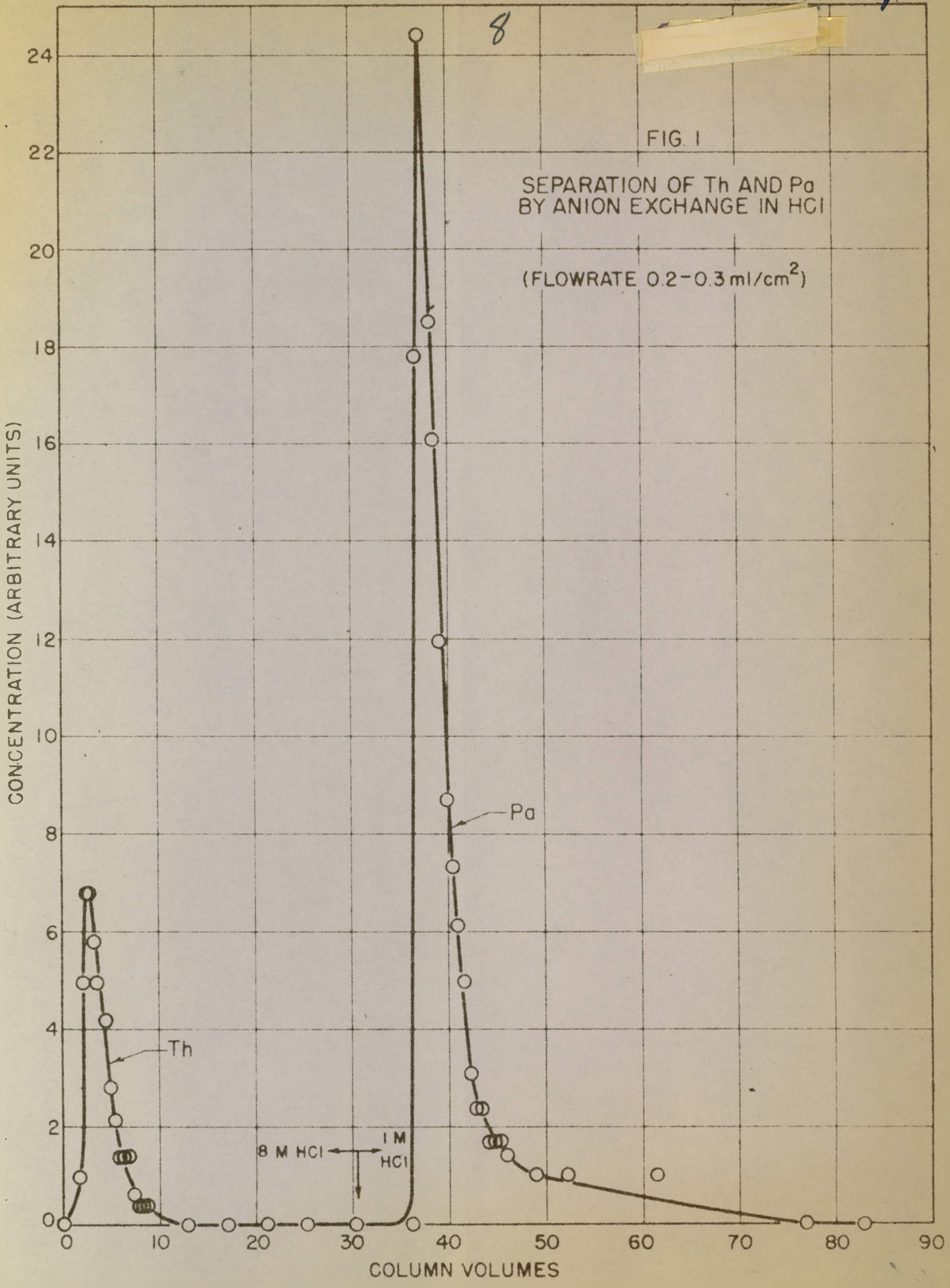

FIG. 1

SEPARATION OF Th AND Pa BY ANION EXCHANGE IN HCl

(FLOWRATE 0.2–0.3 ml/cm^2)

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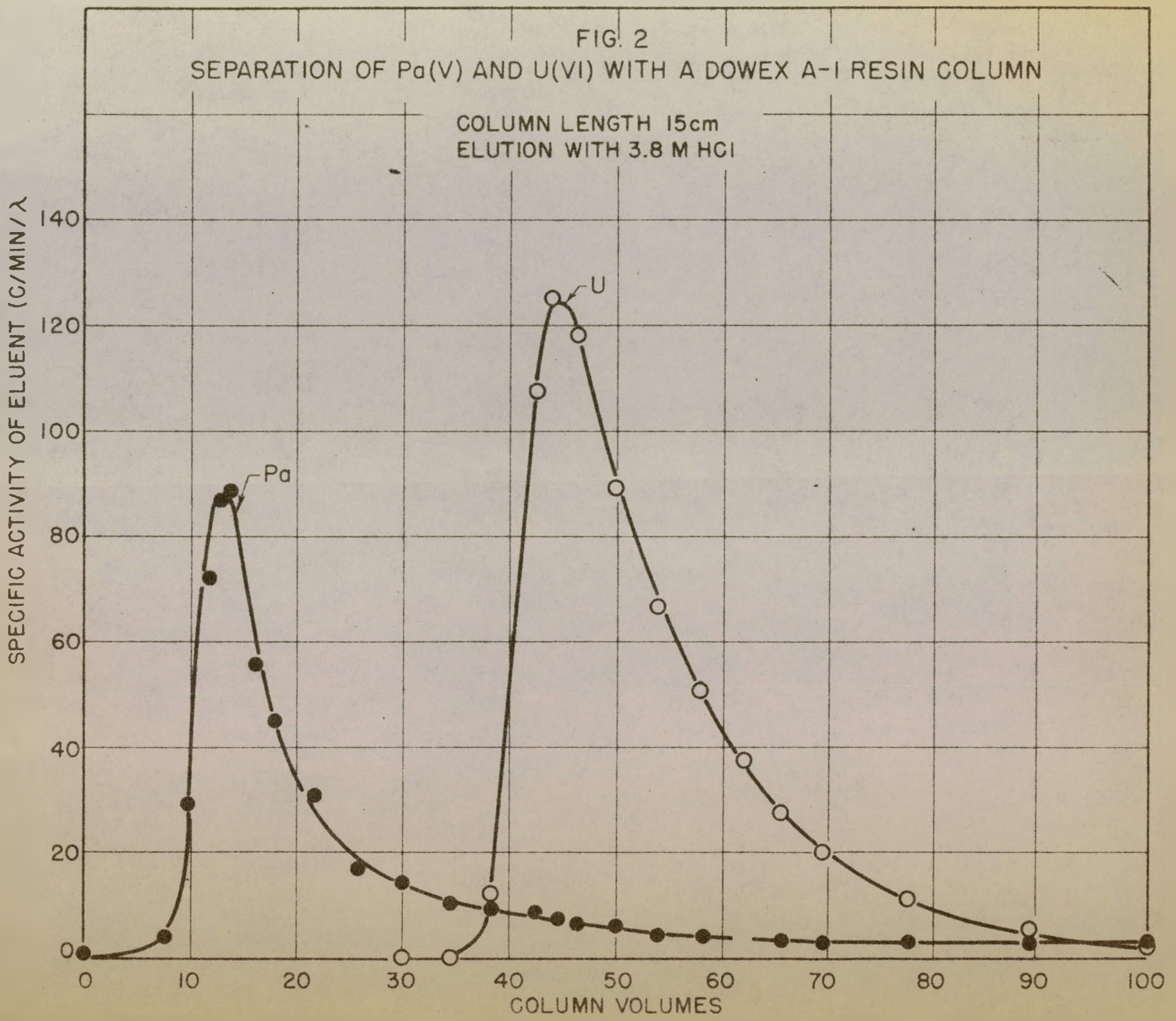

FIG. 2
SEPARATION OF Pa(V) AND U(VI) WITH A DOWEX A-1 RESIN COLUMN