

ION EXCHANGE PROCEDURES

VI. CATION EXCHANGE OF Ac(III) AND Fr(I) IN HCl AND HClO₄ SOLUTIONS;
ISOLATION OF ²²⁷Ac FROM ²³¹Pa AND ²²⁷Ac DAUGHTERS*,**

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In a previous paper² cation exchange adsorption functions of most elements were reported for a wide range of HCl and HClO₄ concentration; Ac(III) and Fr(I) were not included since, at the time, we did not have tracers of these elements on hand. Recently we obtained*** a few mg of ²³¹Pa, which decays to 22 y ²²⁷Ac and 22 m ²²³Fr (AcK), and examined the adsorption behavior of these elements. The present paper reports the results and describes a cation exchange procedure for isolating ²²⁷Ac from milligram amounts of ²³¹Pa and from members of the ²²⁷Ac decay chain, particularly 18.2 d ²²⁷Th, 11.7 d ²²³Ra, 36 m ²¹¹Pb, and 2.16 m ²¹¹Bi.

RESULTS AND DISCUSSION

1. Adsorption functions of francium (I) and actinium (III) (Fig. 1)

Adsorption of Fr(I) from 1 to 12 M HCl and HClO₄ solutions was measured by the band elution method. Small aliquots of purified ²²⁷Ac (in secular equilibrium with ²²³Fr) in appropriate HCl or HClO₄ solutions were added to 0.28 cm² × 3 cm columns of Dowex 50-X₄ and then eluted. The actinium tracer was purified before use as described in Section 2. The elution band for Fr(I) was identified by decay rate measurements and gamma spectroscopy.

Adsorbability of Fr(I) in 1 to 12 M HCl and 1 to 12 M HClO₄ is low, D_v (amount per liter bed/amount per liter solution) is 5.7 and 3.0 for 1 M HCl and 1 M HClO₄, respectively; at higher HCl and HClO₄ concentrations, adsorption decreases and eventually becomes negligible. The adsorption behavior of Fr(I) in HCl and HClO₄ solutions is, as expected, very similar to that of Cs(I)².

Adsorption of Ac(III) from HCl and HClO₄ solutions was measured by the column method when adsorbability was low ($D_v < 10$) and by batch equilibration when $D_v > 10$; the solutions were assayed by β -counting. The ²²⁷Ac was purified immediately before equilibration and short equilibration times (ca. 12 h) were used so that errors from growth of β -emitting daughter activities were minimized.

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** For Part V see ref. 1.

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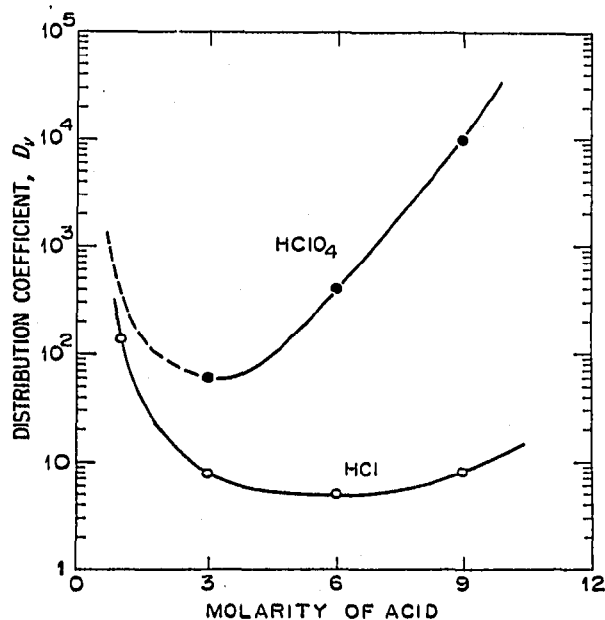


Fig. 1. Adsorption of Ac(III) from HCl and HClO_4 solutions (Dowex 50-X₄, 25°).

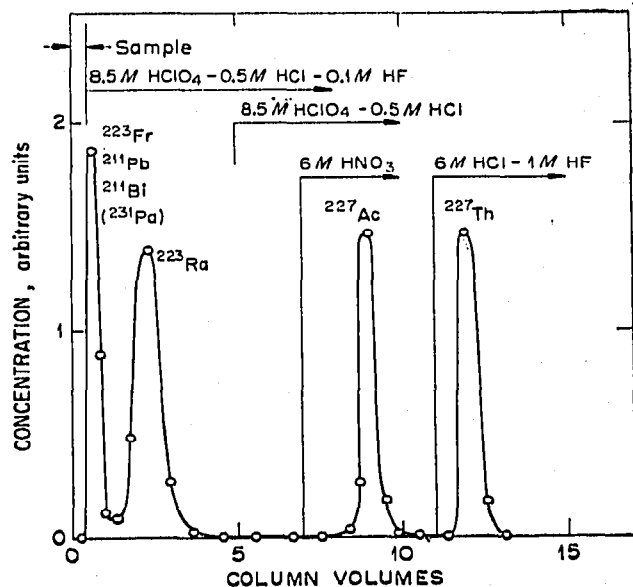


Fig. 2. Isolation of ^{227}Ac by cation exchange (Dowex 50-X₄, -400 mesh, 50°).

The results are shown in Fig. 1, a semi-log plot of D_v versus molarity of acid. In HCl, adsorbability decreases with increasing acid concentration to a shallow minimum, $D_v = 5$, near 6 M HCl, and then increases slowly; these data confirm the results of DIAMOND, STREET AND SEABORG³ with a similar Dowex 50 resin. In HClO_4 , Ac(III) is strongly adsorbed at all HClO_4 concentrations; adsorbability increases rapidly with increasing M HClO_4 from a minimum adsorption, $D_v = 60$, near 3 M HClO_4 to $D_v = 10^4$ near 9 M HClO_4 .

2. Isolation of ^{227}Ac

About 3 mg of ^{231}Pa as the hydroxide was dissolved in 1 ml of concentrated HF in a Teflon evaporating dish and the solution was evaporated to a volume of *ca.* 0.5 ml. The solution was taken up in 1 ml of 0.5 M HCl-0.5 M HF, warmed, and added to a 0.28 cm² × 5 cm column of Dowex 50-X₄ (-400 mesh) which had been pretreated with 0.5 M HCl-0.5 M HF. On elution with 3 column volumes of the same solvent, Pa passed through the column, presumably as a negatively-charged fluoride complex, while Ac(III) and the decay products, ^{223}Ra and ^{227}Th , were adsorbed. The column was treated with 6 M HCl-1 M HF; this medium removes Ra(II) and Ac(III) as well as Th(IV).⁴ Approximately 10 column volumes are necessary for complete elution of Ac(III). Subsequent work showed that 6 M HNO_3 would have been a better eluting agent for Ac(III), as further described below.

The Ac fraction was placed in a Teflon evaporating dish; one ml of concentrated HClO_4 was added, and the solution evaporated to a volume of *ca.* 0.1 ml. The residue was taken up in 0.5 ml of warm 8.5 M HClO_4 -0.5 M HCl-0.1 M HF and added to a 0.28 cm² × 4 cm column of Dowex 50-X₄ (-400 mesh) in a water jacket at 50°. The eluting solution contained HF to assure complexing and elution of possible residual ^{231}Pa ; HCl was present to assure rapid elution of Pb and Bi daughters as chloride complexes². In separate equilibration experiments at 25° it was established that

$D_v = 510$ for Ac(III) in $8.5 M HClO_4-0.5 M HCl-0.1 M HF$, indicating that addition of small amounts of HCl or HF do not seriously reduce the adsorbability of Ac(III) at high $M HClO_4$. On elution with the acid mixture, ^{223}Fr , ^{211}Pb and ^{211}Bi appeared, as expected, in the first column volume of effluent while ^{223}Ra eluted in a sharp band near 2.3 column volumes as shown in Fig. 2. The Ra elution band was corrected for ^{223}Fr activity which continuously eluted and "contaminated" the effluent.

The ^{227}Ac was removed in a sharp band with $6 M HNO_3$, and ^{227}Th , with $6 M HCl-1 M HF$. Before removing actinium, the column was treated with 2 column volumes of $8.5 M HClO_4-0.5 M HCl$ to remove HF, thus avoiding possible partial elution of Th(IV) during elution of ^{227}Ac with $6 M HNO_3$. The separated ^{227}Ac was analysed immediately by β and α counting (pulse analysis). The ratio of β to α counts and the α -spectrum were as expected and indicated the actinium was radiochemically pure for all practical purposes.

The method described here is similar, in principle, to the cation exchange method of CABELL⁵ in which selective elution of the decay products, Fr, Pb, Bi and Ra is accomplished with $2 M HCl$ and $3 M HNO_3$ solutions; Ac is eluted with $6 M HNO_3$ as in our method. Use of a concentrated $HClO_4-HCl$ medium appears preferable for the initial adsorption step since Ac(III) is much more strongly adsorbed from this medium, relative to Pb, Bi and Ra, than from HCl or HNO_3 solutions.

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SUMMARY

The cation exchange behavior of Ac(III) and Fr(I) in HCl and $HClO_4$ solutions is described and a method for isolating ^{227}Ac from its daughters and from ^{231}Pa is presented.

REFERENCES

- ¹ F. NELSON, *J. Chromatog.*, 16 (1964) 403.
- ² F. NELSON, T. MURASE AND K. A. KRAUS, *J. Chromatog.*, 13 (1964) 503.
- ³ R. M. DIAMOND, K. STREET, JR. AND G. T. SEABORG, *J. Am. Chem. Soc.*, 76 (1954) 1461.
- ⁴ T. MURASE, E. L. LIND AND F. NELSON, *J. Chromatog.*, 14 (1964) 478.
- ⁵ M. J. CABELL, *Can. J. Chem.*, 37 (1959) 1094.