with 0.05 N sodium hydroxide in 60% ethanol at room temperature in a nitrogen atmosphere for ten minutes resulted in replacement of halogen by a hydroxyl group. Acetylation yielded the diacetate of Reichstein's Compound P, m. p. 206–207°; $[\alpha]^{25}$D +48° (chloroform).

The preparation of Reichstein's Compound S was achieved by the following reactions: 3α-formoxy-17α-hydroxypregnan-20-one (m. p. 184–185°; $[\alpha]^{34}$D +68° (ethanol), $C_{22}H_{34}O_4$, calcd.: C, 72.89; H, 9.45; found: C, 73.00; H, 9.63) was brominated as in the preceding experiment yielding the 21-bromo compound as a solvate, m. p. 188–190°; $[\alpha]^{35}$D +75° (ethanol). The formate was converted to the hydroxy compound, m. p. 202–204°, with methanol and dry hydrogen chloride at 5° for fourteen hours. Oxidation of $3\alpha,17\alpha$-dihydroxy-21-bromopregnan-20-one with N-bromoacetamide yielded 17α-hydroxy-21-bromopregnan-3,20-dione, m. p. 203–204°; $[\alpha]^{33}$D +81° (ethanol); $C_{21}H_{31}O_3Br$, calcd.: C, 61.31; H, 7.60; Br, 19.43; found: C, 61.02; H, 7.65; Br, 19.59. Hydrolysis of the halogen was accomplished by the procedure described above and, without isolation, the reaction product was acetylated, yielding 21-acetoxy-17α-hydroxypregnan-3,20-dione, m. p. 195–197°; $[\alpha]^{32}$D +81° (ethanol). Bromination in acetic acid yielded the 4-bromo derivative (m. p. 196–203°; $[\alpha]^{36}$D +83° (chloroform); $C_{23}H_{33}O_5Br$, calcd.: Br, 17.03; found: Br, 17.62) which was dehydrobrominated by a modification of the Mattox and Kendall[2] procedure to yield Reichstein's Compound S acetate, m. p. 237–241°; $[\alpha]$D +116° (acetone); ϵ_{2410} = 17,400 (methanol).

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           RECEIVED AUGUST 19, 1949

(2) Mattox and Kendall, THIS JOURNAL, **70**, 882 (1948).
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SEPARATION OF ZIRCONIUM AND HAFNIUM WITH ANION EXCHANGE RESINS[1]

Sir:

During the course of an investigation of the behavior of negatively charged metal complexes on anion exchange resins, an attempt was made to separate zirconium and hafnium. These elements are generally considered to form negatively charged complexes[2] with certain complexing agents, particularly fluoride and oxalate ions. These elements, furthermore, are generally believed to be in true solution (rather than colloidal solutions) only if they are in the form of ionic complexes.

(1) This document is based on work performed under Contract No. W-7405 eng. 26 for the Atomic Energy Commission at Oak Ridge National Laboratory.
(2) Gmelin's "Handbuch der anorganischen Chemie, Hafnium," Verlag Chemie, Berlin, 1941.

A separation based on their ability to form negatively charged complexes thus would have the advantage of being specifically designed for operation under conditions where true solution is most probable and complications due to hydrolysis (colloid formation or precipitation) minimized.

The experiments which have been carried out have demonstrated that separation of Zr(IV) and Hf(IV) by anion exchange is feasible, although the separation achieved is by no means at its optimum. Experiments are now under way to improve the efficiency of separation.

Partial separation of Zr(IV) and Hf(IV) at room temperature was achieved using a 107-cm. column of 200–230-mesh Dowex-1 (a quaternary amine anion exchanger) of 0.0226 sq. cm. cross section, and a mixture of 0.5 M hydrofluoric acid–1.0 M hydrochloric acid as eluent. Flow rates of *ca.* 0.3 ml./sq. cm./min. were used. Under these conditions elutions are relatively rapid (complete elution in *ca.* one and one-half days). The experiments were carried out with tracer concentrations of zirconium and 0.2 mg. of hafnium, using Zr^{95} (β-emitter, $T_{1/2}$ = 65 days[3]) and Hf^{181} (β-emitter, $T_{1/2}$ = 55 days[3]) as tracers. Zirconium and hafnium were identified radiochemically and in particular the hafnium content of the various elution fractions was determined by delayed coincidence counting taking advantage of the metastable daughter Ta^{181} (γ-emitter, $T_{1/2}$ = 20μsec.[4]) of Hf^{181}.[5]

The results of a typical experiment are shown in Table I. It may be noticed that the earlier fractions are highly depleted of hafnium, while the last fractions are practically pure hafnium.

TABLE I

SEPARATION OF ZIRCONIUM AND HAFNIUM IN 1.0 M HCl–0.5 M HF

Column length 107 cm., average flow-rate 0.29 ml. cm.$^{-2}$ min.$^{-1}$

No.	Vol., ml.	Spec.[a] act.	Rate[b]	%[c] Hf	No.	Vol., ml.	Spec.[a] act.	Rate[b]	%[c] Hf
4	2.20	16.8	0.08	0.4	9	0.29	510	17	79
5	0.40	290	0.7	3	10	.31	321	22[d]	>95
6	.32	580	1.9	9	11	.31	147	21	>95
7	.27	616	6.6	31	12	.43	30.7	24	>95
8	.31	609	12	56	13	.45	3.3	19[d]	>95

[a] c/min./λ. [b] Coincidence rate per 1000 c./min. [c] Calculated on an activity basis. The initial solution had approximately equal activities of zirconium and hafnium. [d] Radiochemical analyses by S. A. Reynolds did not show presence of Zr^{95}. Estimated purity of the hafnium fractions according to these analyses is better than 95%.

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           RECEIVED JULY 25, 1949

(3) Information from G. T. Seaborg and I. Perlman, "Table of Isotopes," *Rev. Mod. Phys.*, **20**, 585 (1948).
(4) S. DeBenedetti and F. K. McGowan, *Phys. Rev.*, **70**, 569 (1946).
(5) We are indebted to Mr. F. K. McGowan for assistance in the coincidence counting and for the use of his delayed coincidence circuit.