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EFFECTIVE SEPARATION OF HAFNIUM(IV) FROM ZIRCONIUM(IV) AS PYRIDINIUM TERNARY HETEROPOLY SALTS

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The remarkable difference was observed between Zr(IV) and Hf(IV) in the formation of pyridinium ternary heteropoly salts. Separation of Hf(IV) from Zr(IV) using this simple precipitation reaction was examined.

Both zirconium and hafnium have the $(n-1)d^2ns^2$ electron configuration. In spite of the great increase in atomic number, the atomic and ionic radii of hafnium are very close to those of zirconium. This leads to the exceptional similarity between zirconium and hafnium. So hafnium is always associated with zirconium and their separation from each other remained a challenge to analytical chemists for long years. Separation methods adopted were mainly those of using ion-exchange or solvent extraction techniques(1). During the course of the synthesis and the equilibrium studies of ternary heteropoly complexes, the authors found the remarkable difference between Zr(IV) and Hf(IV) in precipitating reaction. This paper reports these results and also refers to the possibility of their separation from each other by a simple precipitating procedure.

The group IV A transition elements(Ti(IV) and Zr(IV)) interact with molybdophosphate. The yellow color of molybdophosphate solution is enhanced in the presence of these elements. Ti(IV) and Zr(IV) could be determined spectrophotometrically by using their formation reaction of ternary molybdophosphate complexes(2-4). Collection of Ti(IV) and Zr(IV) from aqueous solutions was succeeded by precipitating as pyridinium ternary molybdophosphate salts(5). Hf(IV), however, does not produce the same precipitation as Zr(IV) under this condition. This different behavior in the precipitation reaction may suggest the successful separation from each other.

To the solution of pH 1 containing 1×10^{-5} mole metal ion (Zr(IV) or Hf(IV)) were added 20 ml of a 2.5×10^{-2} M molybdophosphate solution of pH 1. After 1 h., which suffices for complete formation of the ternary heteropoly complex, 10 ml of a 0.5 M pyridinium solution adjusted to pH 1 was added dropwise. A yellow pyridinium molybdophosphate salt was precipitated. The precipitate formed was filtered on a filter paper (Toyo No. 5c), and then washed with a solution of pH 1 containing pyridine. The metal ion remaining in the mother liquor was determined spectrophotometrically by using Arsenazo III method in both cases of Zr(IV)(6) and Hf(IV)(7). For various acidic solutions, the same precipitation procedure was performed. The results obtained were shown as curves of collection yields in Fig. 1. In the solutions of pH 5 - pH 2, both Zr(IV) and Hf(IV) show the same precipitation behavior, which is correlated well to the formation of ternary heteropoly complexes in aqueous solution.(4) But in the solutions of below pH 2, the remarkable difference is observed between Zr(IV) and Hf(IV). In contrast with the complete precipitation of Zr(IV), most of Hf(IV) are flowed into mother liquor in these acidic regions. Especially at a 1 M $HClO_4$ solution, 78.7 % of Hf(IV) are eluted out. In 2 M and 3 M acid solutions, the increase in the collection yields in the precipitate of Hf(IV) may be due to the formation of hafnium phosphate which is less soluble than zirconium phosphate. The effective separation may be expected in the solutions of pH 0.8 - 1 M perchloric acid as shown in Fig. 1. In 1 M perchloric acid solution containing both 0.91 mg Zr(IV) and 1.79 mg Hf(IV), same precipitating procedure was examined by using ^{181}Hf as a tracer. The data were given in Table I. In spite of the coexistance of Zr(IV), most of Hf(IV) remain in the solution. The recovery of Hf(IV) amounts to 82.4 % as a mean value in the twice experiments. If the precipitate thus obtained is decomposed by addition of alkaline solution, Zr(IV) precipitates as zirconium hydroxide.

The reason why the chemical behavior is so different between both complexes has not been cleared yet completely. It may be assumed that the dissociation of molybdohafnophosphate is more appreciable than that of molybdozirconophosphate, and that the solubility of the pyridinium salt of molybdophosphate must be much less than that of molybdohafnophosphate. The addition of pyridinium solution in acidic molybdohafnophosphate solution may produce mainly the precipitation of binary heteropoly (molybdophosphate), resulting in the dissociation of Hf(IV) from ternary heteropoly complex. Results of the further studies on equilibrium of ternary heteropoly complexes will be published in a separate paper.

Table I. Experiments for the separation of Hf(IV) from Zr(IV)

Sample	Taken (mg)	Found in soln. (mg)	Recovery(%)
Zr(IV) a)	0.91	0.0018	0.2
Hf(IV) a)	1.79	1.41	78.7
Zr(IV) + Hf(IV) b)	Zr(IV)(0.91)+	Zr(IV)(not determined)	
	Hf(IV)(1.79)+	Hf(IV)(1.45) c)	81.2
	^{181}Hf (trace)	Hf(IV)(1.50) c)	83.6

a) Spectrophotometric determination by Arsenazo III method

b) Radio chemical trace analysis by ^{181}Hf

c) twice experiments

Experimental Condition

Molybdophosphate soln. 2.5×10^{-2} M 20 ml;

Pyridinium soln. of 1 M $HClO_4$ 0.5 M soln. 10 ml;

Acidity of the soln. 1 M $HClO_4$; Total soln. 50 ml;

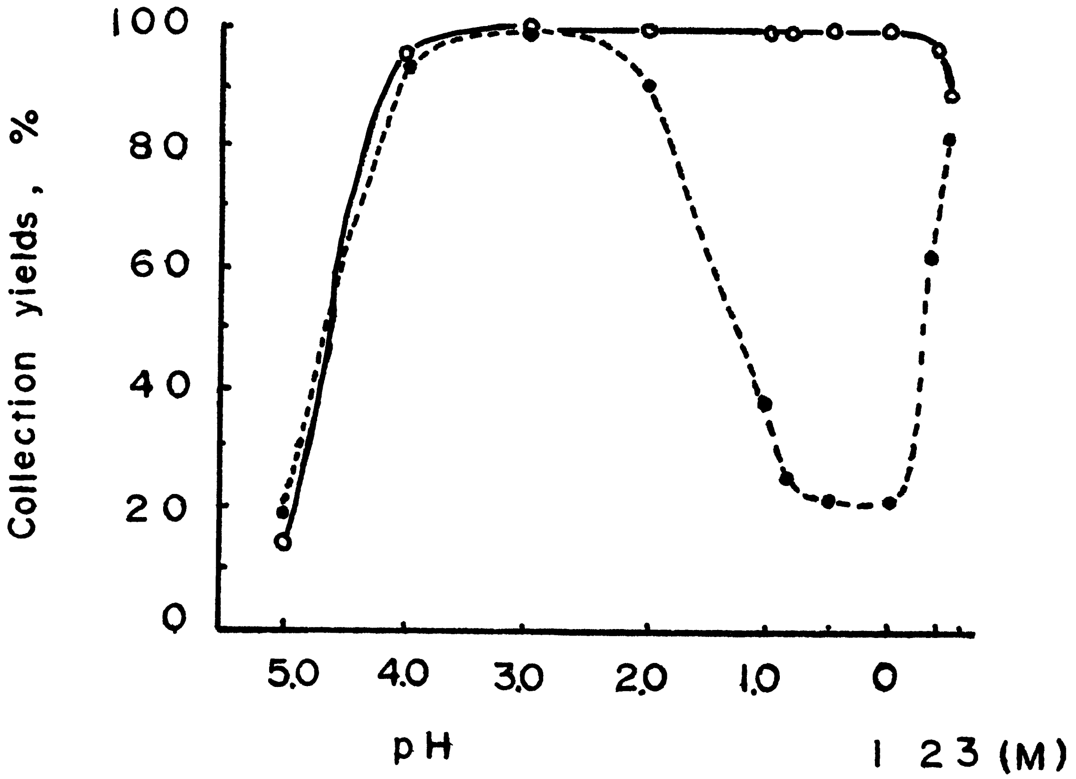

Fig. 1 Influence of acidity on the collection of zirconium(IV) and hafnium(IV)

○	solid line	Zr(IV)
●	dotted line	Hf(IV)

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