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SÔBRE A SEPARAÇÃO DE ZIRCONIUM DE HÁFNIO COM O USO DE TRIFOSFATO DE SÓDIO

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INTRODUCTION

The complexing action of sodium triphosphate has been studied by Frankenthal, Roberts and Neuberg(1) who observed that various cations will form stable solutions with an excess of that reagent. Audrieth and Giesbrecht(2) have shown that elements from the rare earth group will, also, form complexes with sodium triphosphate. Subbaraman, Rajan and Gupta(3) have shown that by using this property of forming complexes with rare earths it is possible to separate some elements of that group by using ion-exchangers and a solution of sodium triphosphate as eluant. The complexes of zirconium IV and zirconyl ions with sodium triphosphate, as well as the ones of thorium IV and uranyl, have been studied by Giesbrecht and Vicentini (4)(5).

The results obtained by working with zirconium IV and zirconyl ions with triphosphate(4) as well as the ones published by Hevesy(6) and Larsen, Fernelius and Quill with phosphate(7), indicated that a separation of zirconium and hafnium, by using sodium triphosphate, might be achieved.

Solutions of zirconium sulphate or hafnium sulphate treated with sodium triphosphate will form unstable solution in which a precipitation will start after a certain time; the relation between hafnium and zirconium in the precipitate is not the same as the one in the original sulphate solution. Preliminary experiments had shown that the proportion of hafnium in the precipitate would always be larger than in the solution. In this way an enrichment of hafnium could be obtained in the insoluble phase and of zirconium in the soluble one.

In a previous paper(4) it was observed that the precipitate obtained from solution of zirconium sulphate with sodium triphosphate had the formula . . . . $(ZrO)_5(P_3O_{10})_2Na_5P_3O_{10}\ 11.5\ H_2O$. The nature of the corresponding precipitate for hafnium has not yet been determined; however, it is highly probable that the formula would be similar to the one for the zirconium compound.

In order to investigate the behaviour of the system zirconium and hafnium sulphates-sodium triphosphate, zirconium and hafnium were labelled with their respective radioisotopes, by irradiating the oxides of zirconium and hafnium in a thermal neutrons flux of about 10^{12} neutrons/sec.cm^2 during a period of time that would vary between three and six hours. Measurements of the irradiated samples were carried out by gamma spectrometry and quantitative determinations were made by measuring the height of the photopeaks of hafnium-181 (0.133 Mev) and zirconium-95 (0.72Mev).

Chemicals

Analytically pure zirconium sulphate $Zr(SO_4)_2 4H_2O$ (British Drug Houses Ltd.) with (3.77 ± 0.03)% of hafnium oxide was used. The percentage of hafnium was determined by activation analysis, as described below.

Sodium triphosphate hexa-hydrate, $Na_5P_3O_{10}.6H_2O$, (Victor Chemical Corp. Chicago, Illinois) was further purified by the method described by Watters, Loughram and Lambert(8) and the purity checked by paper chromatography.

Hafnium oxide (Johnson Matthey, London)98% purity was used. All other chemicals were of analytical grade.

Apparatus

For gamma scanning, a one-channel pulse analyzer (Instituto de Energia Atômica) was used; a linear amplifier (Technical Measurement Corp.), Model A1-4A, a decimal scaler, Model 181-A, and a sodium iodide-thallium well activated scintillation crystal, Model XT-100 (both from Nuclear Chicago Corp.), were also used. The gamma-counting system was standardized by using lead-210 (0.047 Mev), cadmium-109 (0.087 Mev), tin-113 (0.393 Mev), and cesium-137 (0.662 Mev) sources.

Activation analysis of the hafnium content on the starting material

A solution of zirconium-hafnium sulphates was prepared. The hydroxides were precipitated by adding ammonium hydroxide, filtering and washing the precipitate with a dilute solution of the precipitant up to a negative test for sulphate. The hydroxides were dried and two aliquots were prepared for irradiation; to one of the samples hafnium oxide was added and the samples were irradiated in a flux of thermal neutrons of 10^{12} neutrons/sec.cm^2 for three hours. The percentage of hafnium oxide was then determined by the relation:

$$\%HfO_2 = \frac{C_1 P}{C_2 P_1 - C_1 P_2} \, 100 \qquad (1)$$

where P_1 and P_2 are the weights of samples <u>1</u> and <u>2</u>, and C_1 and C_2 the activities, in counts per minute, of the samples; P is the weight of the standard hafnium oxide added to sample 2. The activities were determined at the photopeaks for Hf-181(0.133Mev).

By taking samples corresponding to P_1 = 0.18086 grams, P_2 =0.23611 grams and P=0.00228 grams and by irradiating them as mentioned before, the values C_1= 29,743 counts per minute and C_2 = 48,729 counts per minute were obtained for the activities of samples 1 and 2. By substituting these values in formula (1) the percentage of hafnium in the zirconium sulphate, expressed as hafnium oxide, turned out to be (3.77 ± 0.03)%.

<u>Experimental</u>

All the experiments were carried out with the proportion of zirconium sulphate to sodium triphosphate, in the solution, equal to one to two i.e. $Zr(SO_4)_2\ 4\ H_2O/Na_5P_3O_{10}\ 6\ H_2O = 1/2$.

The solutions were mixed and left standing at room temperature. After the required amounts of time the precipitate was filtered and dried under an infrared lamp. The filtrate was treated with sodium hydroxide and the resulting precipitate was also filtered and dried in the same way. Both precipitates were transferred to plastic vials and counted in the well scintillation crystal. The activities of the zirconium-hafnium precipitate and of the filtrate (obtained with sodium hydroxide)were determined on the photopeaks for hafnium and for zirconium.

<u>Procedure</u>

3.6 grams of zirconium sulphate tetra-hydrate were dissolved in 25 milliliters of water. This solution was added to 75 milliliters of a solution containing 10 grams of sodium triphosphate and the mixture was agitated for one hour. It was then left standing for five days, at room temperature, when the precipitate formed was separated by centrifugation and washed twice with 10 milliliters of a 10 per cent solution of ammonium chloride. The supernatant and the washings were treated with a concentrated solution of sodium hydroxide until no more precipitation occurred. This last precipitate was also separated by centrifugation and both precipitates were dried and transferred to plastic vials for counting. The numerical data obtained on two sets of experiments, carried out as described, are presented in Table I.

TABLE I

Percentage in each fraction						
	Hf			Zr		
			Average			Average
Precipitate	55.7	56.2	56.0	28.2	30.9	29.5
Filtrate	44.3	43.8	44.0	71.8	69.1	70.5

Dependence of zirconium-hafnium phosphate fractionation on time

In order to check the relative proportion of hafnium and zirconium as a function of time, after the formation of the precipitate had already started, experiments were planned in such a way that samples of precipitate and filtrate would be removed from time to time; the activity in both fractions was determined as described. Table II gives the results obtained for the temperature of 25°C.

TABLE II

Fractionation of hafnium-zirconium as a function of time

Sample	Ageing time (hours)	Percentage of starting material in each phase Hf	Zr	Total percentage of starting material	Composition of precipitate, in percentage Hf	Zr
1	53	39.8(x) 60.2	25.4 74.1	26	5.8	94.2
2	71	47.9 52.1	29.6 70.4	30	6.0	94.0
3	114	57.0 43.0	34.7 65.3	35	6.0	94.0
4	168	62.5 37.5	42.3 52.7	42	5.3	94.7
5	191	66.0 34.0	49.0 51.0	49	5.1	94.9
6	287	70.4 29.6	49.8 50.2	50	5.3	94.7
7	451	73.0 27.0	48.8 51.2	49	5.4	94.6

(x) At each time the first number refers to "precipitate" and the second to "filtrate."

Discussion

The hafnium enrichment in the precipitate fraction, indicates that the use of sodium triphosphate may be useful for a first fractionation on the classical separation problem of hafnium-zirconium, specially taking into account that sodium triphosphate is a low cost chemical. As far as price is concerned, the same is valid for the sodium hydroxide and sulphuric acid used for the recovery of the hafnium-enriched phosphate or the zirconium-enriched sulphate. Larger quantities of zirconium sulphate, of the order of one kilogram, are now being processed by using the described method with the aim of obtaining pure fractions of hafnium or zirconium. The first results indicates an enrichment in the same way as when working with small amounts of material.

The question of the mechanism of the observed enrichment may be raised; it could, in principle, be ascribed to a lower solubility of the hafnium phosphate compound or to a kinetic effect with the hafnium phosphate forming more rapidly than the corresponding zirconium compound.

The small variations observed in the percentage of hafnium in the precipitate (column 6 in Table II) do not allow a definite conclusion that a larger hafnium enrichment is obtained at the end of three to five days of ageing. Within the accuracy of the present work it is more reasonable to ascribe the hafnium enrichment, in the solid phase, to a lower solubility of the hafnium phosphate, as compared to the zirconium phosphate, rather than to a higher rate of formation of hafnium phosphate

It is interesting to note that preliminary experiments have shown that when a mixture of zirconyl and hafnyl chlorides was used as a starting material in lieu of the sulphates, treatment with sodium triphosphate produced no observable enrichment.

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