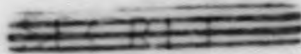


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PROGRESS REPORT

Problem Assignment 263-X61C

PREPARATION OF CARRIER FREE Zr-Cb TRACER

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CARRIER FREE Zr AND Cb TRACER

Abstract

A rapid procedure for the preparation of very pure carrier-free Zr and Cb tracer involves the chloroform extraction of the cupferrides of Zr and Cb activities from process solutions. Zr and Cb form very stable chloroform soluble cupferrides in acid solutions (CK-993) and are separated from other fission elements almost quantitatively to yield pure mixture of Zr and Cb activity. A minimum of operations is required and the method is easily adaptable to remote control.

Introduction

To 40% UNH made 6 M in HCl and 0.05 M in SO₂ are added chloroform and freshly prepared 6% cupferron. The final UNH concentration is about 10%. The Zr and Cb activities are extracted by the CHCl₃. A second extraction is performed on the solution again with chloroform and cupferron. The CHCl₃ extracts are combined and the small amount of contaminating activities is practically completely removed by a 6 M HCl wash. This wash also serves to remove considerable amounts of excess cupferron and its decomposition products. The CHCl₃ layer is then treated with a portion of dilute HCl to which a few drops of Br₂ are added. The cupferrides are decomposed and Zr and Cb activities enter the aqueous phase. Boiling this solution helps to remove traces of organic matter from decomposed cupferron, and the Cb and Zr activities are available in dilute HCl with a trace of HBr.

Experimental Procedure

Reagents: 6% cupferron, freshly prepared.
12 M HCl
6 M HCl
6% H₂SO₃
Br₂

An appropriate amount (1) of 40% UNH (such as 11 MR) in a separatory funnel is made 6 M in HCl and 0.05 M in SO₂. A portion of CHCl₃ is added. This is cooled for 5 - 10 minutes in an ice bath. Cold 6% cupferron (2) is added and the system shaken vigorously for 30 seconds. The layers are separated and another portion of CHCl₃ and cold 6% cupferron is added to the aqueous layer and the system is shaken vigorously again for about 30 seconds. The layers are separated. The two CHCl₃ layers are combined and the aqueous layer is discarded.

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Both the CHCl_3 layer (in the separatory funnel) and a wash solution 6 M in HCl (3) and 0.05 M in SO_2 are cooled in an ice bath for about 5 minutes. The two solutions are then combined and an amount of cold cupferron equal to that used before is added. After shaking vigorously for 30 seconds the layers are separated and the aqueous phase is discarded.

To the CHCl_3 layer in a separatory funnel an aqueous portion 6 M in HCl is added (4). Several drops of Br_2 are added and the system is shaken vigorously for several minutes at 10 minute intervals. After an hour the layers are separated and the CHCl_3 layer is discarded (5). The aqueous layer is boiled until the solution is only slightly colored (6).

Notes:

(1) For 5 ml of 11 MR solution, from the Clinton Plant dissolver, 1.2 ml of 6% cupferron, 5 ml of water, and 10 ml portions of CHCl_3 have been used successfully.

(2) It is necessary to perform the extraction as rapidly as possible when oxidizing materials are present in the process solution (e.g. nitrites and nitrates) because of the instability of the cupferron. In process solutions containing no oxidant, cooling will be unnecessary, and SO_2 addition can be neglected.

(3) With 5 ml 11 MR 10 ml 6 M HCl is used.

(4) 5 ml of 6 M HCl is used with 5 ml 11 MR.

(5) Separation of the two layers may be accomplished efficiently by drawing off most of the original CHCl_3 layer and then adding fresh CHCl_3 and repeating the withdrawal. This may be done three or four times so that when the aqueous phase is finally collected very little organic material from the original CHCl_3 phase will be present to contaminate the product.

(6) If the presence of oxalic acid in the tracer solution is not objectionable, the solution may be made 0.5% in $\text{H}_2\text{C}_2\text{O}_4$ before boiling. The presence of oxalic acid prevents strong adsorption of the activities on the glass walls. Both Zr and Cb are readily adsorbed on glassware from the CHCl_3 - cupferron solution. It is a good practice to store Cb tracer as an oxalate solution and destroy oxalic acid by fuming with concentrated HNO_3 just before use.

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Discussion

A. Yield Determinations. Three separate runs were made in which 11 MR process solution was the starting material. All runs were identical except in the manner of final extraction of activities from the CHCl_3 layer.

In run No. 1, eleven batches of 5 ml each were taken through the above procedure with a 15 minute H_2O_2 final extraction from CHCl_3 being used instead of bromine. The use of H_2O_2 gave a deeply colored yellow solution and indicated the presence of large quantities of undesirable organic matter. Upon treatment with a few drops of Br_2 and subsequent boiling the yellow color almost completely disappeared. It was also observed that about 28% of the activity remained in the CHCl_3 layer and after standing some hours a few drops of Br_2 in 6 M HCl extracted this residual activity into the aqueous phase almost completely.

Yield tests were made on the H_2O_2 extracted fraction, and 77% of the original Zr activity in the 11 MR was found in the final tracer solution. The yield of Cb in this run was 10%.

In run No. 2 five ml of 11 MR was taken through the procedure with a 10 minute final extraction with Br_2 . The tracer was only slightly colored. However, it was observed that considerable activity was left in the CHCl_3 layer. Longer contact with Br_2 before extraction with HCl was found to give complete separation.

Analyses indicated a 61% yield of Zr and a 31% yield of Cb.

In run No. 3 two ml of 11 MR was taken through the complete procedure as given herein. The tracer was very slightly colored and no activity remained in the CHCl_3 layer. Test indicated a 56% yield of Zr and a 33% yield of Cb. Since smaller volumes were used in this experiment, a somewhat lower yield was to be expected because of the greater effect of mechanical losses.

B. Purity Tests. (In run No. 1, a La analysis was made on a portion containing 1.3×10^7 gamma counts per minute at 100% geometry, and the isolated La showed no measurable gamma activity. Therefore, the La contamination was less than 0.03% assuming that a maximum of 40 gammas per minute may not have been counted at this low activity level. More than one half-life of La^{140} (40h) elapsed between the preparation of the tracer and the La analysis. Assuming that all the La activity grew from its Ba parent, the maximum amount of Ba contamination that could be present is 0.06%.

In run No. 2, La was shown to be less than 0.1% of the activity while Ba was found to be 0.03% of the total activity. A Ru determination

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on a sample containing 5.4×10^4 gamma counts per minute gave a Ru fraction with no activity. Thus less than 0.07% of the activity was due to Ru.

A Ba analysis on the run No. 3 preparation indicated less than 0.002% Ba to be present. Contamination by Te was tested and found to be less than 0.004%. We are indebted to the Fission Product Analysis Group for a number of analyses.

C. Large Scale Operations. The possibility of adapting the procedure to large scale operations seems very promising. The main problems will be effective stirring and cooling. Preliminary experiments indicate that the use of a nitrogen stream is satisfactory for stirring. Studies on cooling methods are being planned.

D. Summary. The cupferron - chloroform method for the preparation of carrier-free Zr and Cb activities has been shown to be quite specific. A preparation which is better than 99.8 - 99.9% pure is readily obtained and the time required is about $1\frac{1}{2}$ hours. The technique is simple and small laboratory preparations are very easily and quickly performed; good adaptability to remote control is indicated.

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