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ABSTRACT

A continuous extractor for use with a chelating agent has been developed. Specifically, gram amounts of thorium as the nitrate salt have been extracted using a solution of TTA in benzene. One gram of thorium can be extracted in about three hours. The extractor is especially useful for work with very radioactive materials since shielding is simple and most operations are automatic.

A METHOD FOR CONTINUOUS EXTRACTION WITH A CHELATING AGENT

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The use of chelating agents in a variety of extraction methods developed over the past few years has greatly increased the number of possibilities of separating many of the elements.<sup>1</sup> In the field of nuclear chemical separations, especially, "chelating extractions" have made possible very clean-cut separations of many elements in widely varying concentrations --- from macro amounts to tracer amounts.<sup>2,3</sup>

In the field of solvent extraction many different systems for continuous extraction have been devised.<sup>4</sup> Separations using chelating agents have not in general, however, been adaptable to continuous systems. The work reported here arose from the problem of safely separating macro amounts (1-5 grams) of thorium from the highly radioactive fission and spallation products<sup>5</sup> present in tracer quantities after high-energy bombardment of the thorium target material in the Berkeley 184-inch cyclotron. It was especially important that the radium and actinium isotopes be completely recovered from the thorium for this work. In precipitation reactions the bulky precipitate formed carried down large percentages of the radioactive tracer material even with "holdback carriers" present.<sup>6</sup> While several solution and reprecipitation cycles allowed recovery of the desired materials, the operator was exposed to large amounts of radiation in the process. Solvent extraction with "penta-ether" (dibutoxy tetraethylene glycol --- obtainable from Carbide and

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Carbon Chemicals Division, New York City) gave resultant solutions saturated with ammonium nitrate salting agent which was very difficult to separate from the radioactive tracers.<sup>7</sup>

Manual batch extraction with TTA (thenoyltrifluoroacetone)<sup>8</sup> in benzene has been used for thorium on a tracer and milligram scale.<sup>7,9</sup> It was thought that a continuous extractor using this chelating agent would minimize the personal contact and hence the health hazard involved in working with these very radioactive bombardments.

In the procedure described below, the thorium is extracted with TTA from a pH 2.5 nitric acid solution of the thorium target and is then re-extracted into 2 N acid solution in a second container. The thorium is recovered, while most spallation products, including the radium and actinium isotopes remain in the residue with many of the fission products. A solution less acid than pH 2.5 would still allow chelation of thorium, but other products of bombardment would also be chelated and removed from the solution.<sup>9</sup> As thorium is extracted the solution becomes more acid until a pH of about 0.7 is reached. At this point it is necessary to neutralize the solution to pH 2.5 before further thorium extraction can take place.

#### Apparatus

Fig. 1 illustrates the entire continuous extraction apparatus. The extractor consists of a 50 ml sintered glass funnel of medium porosity which has been extended above the sintered disc to a total height of 25 cm by the addition of 50 mm glass tubing. Several "overflow" tubes of 7 mm glass tubing sealed on to the side of the extractor allow the adaption of the extractor to varying amounts of solution to be extracted.

The inlet tube below the sintered glass disk F is connected to the 200 ml chelate reservoir E with flexible tubing. The tubes sealed on to the extractor at G permit the insertion of micro pH electrodes into the solution to be extracted. A small collar of rubber tubing effectively seals the electrodes and tubes. The stopcock at A controls the flow of nitrogen gas which is used to lift the extractant from the extractor to the small trap bulb C where it then falls by gravity into Flask I. The trap bulb eliminates the spattering which would occur if the solution were discharged directly into Flask I. Flasks I and II are standard 500 ml Erlenmeyer flasks with attached "overflow" side tubes of 7 mm glass tubing. Small stirring motors (D) furnish sufficient agitation for the re-extraction and washing taking place in these flasks.

Tygon tubing was used for all connections in the early work with this apparatus. Inasmuch as it was found that this tubing becomes very hard and inflexible upon continued contact with benzene, polyethylene tubing has been used in more recent experiments. All glass in the extraction apparatus is borosilicate glass.

The pH of the extraction mixture was measured with a Beckman Model G pH meter equipped with micro glass and calomel electrodes. pH measurements with these electrodes were necessarily carried out in electrically unshielded areas. Reproducible readings were possible, however, if movement near the electrodes was reduced during measurement.

When more thorium is present than can be extracted in one cycle and neutralization to pH 2.5 is required, the apparatus shown in Fig. 1 can be modified to include a stirrer and an  $\text{NH}_3$  gas inlet tube in the extractor.



The system must remain airtight with these additions.

### Reagents

Thenoyltrifluoroacetone (TTA) molecular weight 222 (obtainable from Dow Chemical Company, 310 Sansome Street, San Francisco, California) was used throughout as the chelating agent. It was dissolved in reagent grade benzene to make a 0.25 M solution. The chelating agent can be re-used several times in the continuous extractor, the principal limiting factor being change in molarity caused by evaporation of benzene.

### Procedure

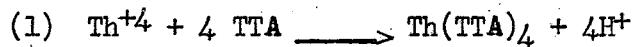
Flask I, the re-extraction flask, is partially filled with 2 N  $\text{HNO}_3$  to strip the thorium from the chelate complex. Flask II, the washing flask, is partially filled with distilled water, to wash out any acid carried over mechanically by the TTA solution from Flask I.

The solution of TTA in benzene is added to the reservoir at E and allowed to partially fill the extractor. The thorium nitrate solution at a pH of about 2.5 is then added to the extractor, the rubber stopper replaced and more 0.25 M TTA solution added to the reservoir at E. The chelating solution is dispersed into fine bubbles upon passing through the sintered glass disc and passes up through the thorium nitrate solution forming the less dense benzene-chelate layer on top. The stopper placed in the top of the extractor insures a closed liquid system. The height of the liquid in the extractor is adjusted by the "draw off" stopcocks at B. When the desired liquid height in the extractor has been attained, the nitrogen gas is turned on at A and one of the stopcocks at B opened. The nitrogen lifts the solution from the extractor into the trap at C.

The height of the reservoir E and the gas pressure through A can be so adjusted that it is possible to lift as much as 10 ml of solution per minute up to C. From the trap the solution flows into Flask I.

Flask I is the re-extracting or stripping flask. Here the chelating agent is stripped of the metal ions in 2 N HNO<sub>3</sub> and the reagent is reconverted to the acid form. Stirring motor D insures good agitation, but should be regulated so that chelating solution overflowing into Flask II will contain no visible bubbles of aqueous solution. In Flask II the chelating agent is washed free of small amounts of occluded nitric acid from the re-extractor. The overflow of this renewed chelate solution runs into the reservoir and the cycle is repeated.

This extraction process will run continuously until due to the reaction in equation (1), the pH changes to a value where chelation of the thorium ions and hence the extraction of the thorium is no longer possible.



For macro amounts of thorium this has been found to occur at a pH of about 0.7. When this pH is reached, the reservoir is stopped off and as much TTA as possible pumped off from the aqueous thorium solution in the extractor by opening the overflow tube nearest the top of the solution. While the solution is agitated the pH is adjusted to about 2.5 by careful addition of NH<sub>3</sub> gas. The reservoir tubing is then opened again and the extraction continued. If the solution is agitated vigorously enough during neutralization to draw bubbles and chelate solution into the aqueous solution or if the NH<sub>3</sub> is added too rapidly a granular precipitate of the ammonium salt of TTA will form and interfere with further chelation. With practice this neutralization can be made in a few minutes.

When the system uses about 200 ml of TTA solution to extract 60 ml of thorium nitrate solution, the thorium extraction (pH change from 2.5 to 0.7) is accomplished in about two hours if the stirring in Flasks I and II is adjusted so as to give good mixing and but little carry-over of aqueous droplets. For such a run the top of reservoir E was about 60 cm above the sintered glass disk and the gas flow was adjusted so that about 10 ml per minute of solvent was lifted to bulb C. The amount of thorium extractable from the aqueous solution is of course dependent upon the pH change of this solution and not upon the total volume of the chelating agent. It was found that if Flask II were not present in the system, the acid carried over from the re-extraction in Flask I reduced the total amount of thorium extractable before neutralization. With no acid carry-over it can be calculated that about 0.7 gm of thorium can be extracted from 60 ml of solution as the pH changes from 2.5 to 0.7. These results have been verified experimentally.

About three hours were required to completely extract a sample containing one gram of thorium with the above system. This included one neutralization.

### Discussion

This extracting system is especially applicable to separations of highly radioactive materials. Since all manipulations are adaptable to remote control and most of the functions are automatic, the extractor can be well shielded as can the re-extracting Flask I. The rest of the system will require little shielding for most separations. For partially shielded systems the only contact need be during the neutralization procedure which requires only a few minutes for every two hours of extraction time.

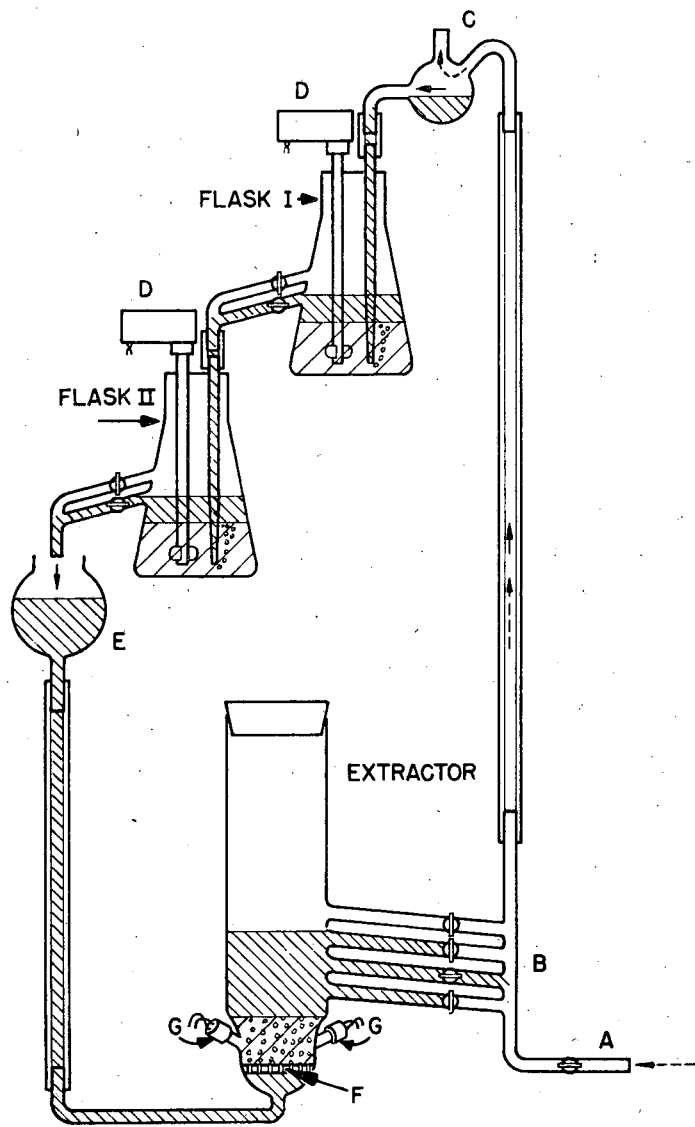
Although this method was developed specifically for the extraction with TTA of macro amounts of thorium from tracer spallation and fission products, it is readily adaptable to many other types of problems -- especially those arising in work with very radioactive solutions. The "air lift" principle of circulating the solvent could be adapted to very small amounts of solutions. Hence the apparatus as presented here could be scaled down to handle smaller amounts of chelating agents. Moreover, it could be scaled up to allow the extraction of larger amounts of material per run. A variety of chelating agents could be used, the only requirement being, of course, that the solution of the chelating agent be lighter than the solution of the extractant and that there be a minimum tendency towards forming emulsions upon stirring. The system could be especially adapted to the separation of materials whose distribution coefficients between the chelating agent and the aqueous medium are rather small, where the continuous extraction would result in a building up of the desired product.

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Fig. 1  
Extraction Apparatus