

RECEIVED BY DTIC DEC 27 1971

UCLA - 12 - 8 49

MASTER

# UNIVERSITY OF CALIFORNIA, LOS ANGELES



LABORATORY OF NUCLEAR MEDICINE AND RADIATION BIOLOGY

CONTRACT NO. AT (04-1) GEN-12

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

## **DISCLAIMER**

**This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.**

## **DISCLAIMER**

**Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.**

THE CARRIER-FREE ISOLATION OF INDIUM FROM SILVER AND  
CADMIUM BY LIQUID-LIQUID EXTRACTION<sup>1</sup>

R. A. Wood, S. T. Wakakuwa, and N. S. MacDonald

Laboratory of Nuclear Medicine and Radiation Biology, and  
Department of Radiological Sciences,  
University of California, Los Angeles<sup>1</sup>

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

<sup>1</sup>These studies were supported by Contract AT (04-1) GEN-12<sup>2</sup> between the Atomic Energy Commission and the University of California.

# THE CARRIER-FREE ISOLATION OF INDIUM FROM SILVER AND CADMIUM BY LIQUID-LIQUID EXTRACTION

**ABSTRACT** An analytical method was developed for the rapid and carrier-free separation of  $2.81d$   $^{111}\text{In}$  produced by the reactions  $^{109}\text{Ag}(\text{He}^4, 2n)^{111}\text{In}$  and  $^{110}\text{Cd}(d, n)^{111}\text{In}$ . The method is based upon the fact that indium in the presence of macro-concentrations of  $\text{Ag(I)}$  and  $\text{Cd(II)}$  preferentially extracts into  $n$ -heptane solutions of bis (2-ethylhexyl) hydrogen phosphate (HDEHP) from aqueous nitric acid media. The  $\text{Ag(I)}$  and  $\text{Cd(II)}$  remain quantitatively in the aqueous phase. The distribution ratios ( $K$ ) vary from greater than  $10^3$  for  $\text{In(III)}$  to less than  $10^{-2}$  for  $\text{Ag(I)}$  and  $\text{Cd(II)}$ . The indium is quantitatively stripped from the solvent phase with  $\text{HCl}$ . The total separation time is less than 10 min. In the present investigation  $K$  has been studied with respect to acid-solvent dependence, equilibration, and back extraction. Optimum conditions for maximum extraction have been determined.

## INTRODUCTION

Clinical applications of radioindium [1] require the use of isotopes with semi-short half-lives (e.g.,  $^{111}\text{In}$ ). These isotopes may be produced by the bombardment of silver or cadmium by charged particles in a cyclotron. Following activation, it is necessary to

- 
1. Cerebrospinal Fluid Scanning with  $^{111}\text{In}$ . P. Matin & D. A. Goodwin. J. Nuclear Medicine 12, 668-672 (1971).

quickly and efficiently separate the radioindium from the silver or cadmium targets.

Separation of indium by liquid extraction techniques has been studied over the past 20 years. Steinbach and Freiser [2] reported on the use of chloroform solutions of acetylacetone. Claassen and Bastings [3] used carbon tetrachloride solutions of 0.2% sodium diethyldithiocarbamate. Sunderman and Townley [4] showed that in acid solutions indium is separated from a number of elements using diethylether and thenoyltrifluoroacetone. Hudgins and Nelson [5] showed that indium is quantitatively isolated by extraction with isopropyl ether from 1M HBr solutions. Irving and Rossotti [6] showed that indium is quantitatively separated from Fe and Be by extraction into ethyl ether from 1.5M HI solutions. The use of acid esters of aliphatic alcohols and phosphoric acids for the extraction of indium was first reported by Scadden and Ballou [7], who showed that indium and quadrivalent tin are extracted by butyl ether solutions of butylphosphoric acid from sulfuric or nitric acid media.

- 
2. J. F. Steinbach and H. Freiser, Anal. Chem. 26, 375 (1954)
  3. A. Claassen, L. Bastings, and J. Visser, Anal. Chem. Acta. 10, 373 (1954)
  4. D. N. Sunderman and C. W. Townley, NAS-NS 3014, pp. 25 (1960)
  5. J. D. Hudgins and L. C. Nelson, Anal. Chem. 24, 1472 (1952)
  6. H. M. Irving and F.J.C. Rossotti, Analyst 77, 801 (1952)
  7. E. M. Scadden and N. E. Ballou, Anal. Chem. 25, 1602 (1953)

Levin [8-12] was the first to report on the extraction behavior of indium by 2-ethylhexyl phosphoric acid from various inorganic and organic acid systems.

Unfortunately, all of these methods are relatively slow, and some require precipitation procedures to isolate the indium. The following report describes the development of a carrier-free procedure for the rapid separation of short-lived indium radionuclides produced by charged particle activation.

#### EXPERIMENTAL

**SOURCE OF REAGENTS** The bis(2-ethylhexyl) hydrogen phosphate and n-heptane were obtained from Eastman Organic Chemicals, Rochester, New York and were used without any further purification. The 50d  $^{114m}\text{In}$ , 260d  $^{110}\text{Ag}$ , and 1.2y  $^{109}\text{Cd}$  radio-tracers were obtained from International Chemical and Nuclear Corporation, Irvine, California. The carrier solutions were prepared from 99+% pure salts of indium, silver and cadmium (as nitrates) obtained from Baker and Adamson Reagent Chemicals, Morristown, New Jersey.

**DISTRIBUTION RATIO (K)** The distribution ratio, defined as the concentration of metal in the organic phase divided by its concentration in the aqueous phase, was determined radiometrically.

Triplicate aliquots of each phase at equilibrium and after centrifugation

- 
8. I. S. Levin, Zhurnal Prikladnae 35, 11, 2368 (1962)
  9. I. S. Levin and V. A. Mekhailov, Don 138, 6f (1961)
  10. I. S. Levin, Zh. Anal. Khim. 18 (1963) 1335; 20 (1965) 452
  11. I. S. Levin, Zh. Prikl. Khim. 25, 2369 (1962)
  12. I. S. Levin and A. A. Shatalova, Dokl. Akad. Nauk, SSSR 16 (1965) 1158

were transferred by volumetric pipette to 1-inch diameter plastic counting cups and evaporated to near dryness under infrared heating lamps. The samples were then gamma assayed in a 9-inch x 9-inch NaI(Tl) well crystal assembly in conjunction with a 512 channel R.C.L. pulse height analyzer. The counting error in all cases was within  $\pm 5\%$  at the 95% confidence level.

**EXTRACTION METHODS** The methods employed in the extraction studies were as follows: Aliquots of  $^{114m}\text{In}$ ,  $^{110}\text{Ag}$  and  $^{109}\text{Cd}$  radiotracers were transferred to 125 ml separatory funnels containing 10 ml of 0.5M  $\text{HNO}_3$ . Five hundred milligrams of silver and cadmium carriers were then added. Equal aliquots of freshly prepared 15 volume % HDEHP-n-heptane were added and the samples mixed for 5 min on a mechanical shaker (200 strokes per min). The phases were separated into 50 ml tubes and centrifuged for 2 min. Aliquots of each phase were mounted and counted by methods previously described. All experiments were run at  $25^\circ \text{C} \pm 2$ .

**EXTRACTION METHODS APPLIED TO CYCLOTRON TARGETS** The targets of silver and cadmium were prepared by electroplating [13] 150 mg of metal on 1/2-in dia circles centered on gold plated copper discs 4-in dia x 1/4-in thick. The silver targets were bombarded with 24 MEV alpha particles for an integrated beam current of 60 microampere-hours. Cadmium targets were bombarded with 12 MEV deuterons for 20 microampere hours. The principal reactions, respectively, were  $^{109}\text{Ag} (\alpha, 2n) ^{111}\text{In}$  and  $^{110}\text{Cd} (d, n) ^{111}\text{In}$ . After removal from the cyclotron

---

13. D. N. Sunderman, Anal. Chem. 29, 11, 1583 (1957)



the metals were dissolved from the target discs with 2 ml of hot 6M  $\text{HNO}_3$  using remote handling techniques. The samples were then stored for 24 hrs to allow decay of 4.3h  $\text{In}^{109}$  and 4.9h  $\text{In}^{110}$  also produced by the bombardments. The samples were then transferred to separatory funnels. The  $\text{HNO}_3$  concentrations were adjusted to 0.5M with water. Equal aliquots of freshly prepared 15 volume % HDEHP-n-heptane were added and the mixtures shaken mechanically for 5 min (approximately 100 strokes per min). The phases were separated and processed as previously described. (In routine production runs the depleted aqueous acid phases are discarded.) The pregnant organic phases were scrubbed 3 times with 5 ml portions of fresh 0.5M  $\text{HNO}_3$  to remove any trace of aqueous phase. The  $\text{In}^{111}$  was then stripped from the organic phases with 3 ml of 12M  $\text{HCl}$  using identical mixing techniques. It is interesting to note that approximately 3 mc of  $\text{In}^{111}$  are produced per run under the conditions described. The only contaminant found with the  $\text{In}^{111}$  in the back-extracts was a trace of  $\text{In}^{114m}$  ( $<0.001\%$ ). A typical gamma ray spectrum of the final product is shown in Fig. 5.

#### RESULTS AND DISCUSSION

**ACID DEPENDENCE** Figure 1 shows variation in K for tracer level  $\text{In}^{114m}$  at aqueous phase hydrogen ion concentrations ranging from 1-22M  $\text{HNO}_3$ . Equal portions of  $\text{Ag}^{110}$  and  $\text{Cd}^{109}$  radiotracers were present in the aqueous fractions. The K values show inverse acid dependence between 1-12M and direct dependence between 12-22M. The inflection of the curve at 12M  $\text{HNO}_3$  is not yet fully understood. However, it is evident that good separations of indium can be made at  $\text{HNO}_3$  concentrations  $\leq 4\text{M}$  or at  $\geq 18\text{M}$ , since K values of 100 yield  $\geq 98\%$

recovery. Levin [14] observed similar inflections of acid dependence curves in the isolation of Ga and Tl from HCl and HBr media into HDEHP systems, as did Kimura [15] in the extraction of other metal systems from HCl into toluene solutions of HDEHP. The K values of  $^{110}\text{Ag}$  and  $^{109}\text{Cd}$  were less than  $10^{-2}$  and remained constant over the whole range of acid concentration tested.

**SOLVENT DEPENDENCE** Figure 2 shows variation in K when  $^{114\text{m}}\text{In}$  in 0.5M  $\text{HNO}_3$  is treated with equal volumes of HDEHP ranging from 5-50 volume % in a diluent of n-heptane. The K values show direct solvent dependence between 1-20 volume % and inverse dependence between 20-50 volume % HDEHP-n-heptane. The decrease in K at solvent concentrations above 20 volume % is not understood, but was independent of mixing time. Comparable solvent effects have been observed by Kimura [16] and Wood and Roscoe [17] in similar solvent systems. The K values for  $^{110}\text{Ag}$  and  $^{109}\text{Cd}$  were less than  $10^{-2}$ .

**EQUILIBRATION STUDIES** Figure 3 shows variation in K for  $^{114\text{m}}\text{In}$  for mixing periods of the phases ranging from 5 sec to 5 min. The mixing periods were started within 1 sec after the addition of the solvent phase. These data show that indium reaches equilibrium in less than 90 sec.

The K values for  $^{110}\text{Ag}$  and  $^{109}\text{Cd}$  were less than  $10^{-2}$  and were independent of mixing time. In similar experiments the mixing rates were decreased to 75 strokes per min. The K value did not significantly

---

14. I. S. Levin, Proceedings of International Conference on Solvent

Extraction Chemistry, John Wiley & Sons, Inc., New York, pp. 243 (1967)

15. K. Kimura, Bull. Chem. Soc. Japan 33, 8, 1038 (1960)

16. K. Kimura, Bull. Chem. Soc. Japan 34, 1, 63 (1960)

17. R. Wood and R. Roscoe, J. inorg. nucl. Chem. 32, 1351 (1970)

change from those observed at 200 strokes per min.

BACK EXTRACTION STUDIES      The back extraction of  $^{111}\text{In}$  from the pregnant solvent phases using HCl was studied. Figure 4 shows variations in  $1/K$  with respect to varying concentrations of HCl ranging from 1-12M. The solvent phases were mixed for 10 min although equilibrium is reached in less than 5 min. The stripping of  $^{111}\text{In}$  from the solvent phases shows direct dependence upon HCl concentration with a maximum in 12M HCl. Spectrometric and radio-analysis of these aqueous fractions showed only a trace of cadmium and silver ( $\leq 0.0001\%$ ).

It is of interest to note that HBr and acidified solutions of 3%  $\text{H}_2\text{O}_2$  were equally efficient in stripping  $^{111}\text{In}$  from the solvent phases.

#### ACKNOWLEDGEMENT

The authors wish to express their gratitude to Dr. F. B. Turner, and Messrs. H. Neeley, R. Birdsall, and R. Van Deusen for their assistance and helpful suggestions during the course of this study.

## LEGENDS

Fig. 1. Variation in  $K$  vs.  $\text{HNO}_3$  concentrations in the aqueous phase into 15 volume % HDEHP in a diluent of n-heptane.

Fig. 2. Variation in  $K$  vs. HDEHP concentrations in the organic phase from an apasing phase of 0.5M  $\text{HNO}_3$ .

Fig. 3. Variation in  $K$  vs. mixing time of aqueous systems containing tracer level  $^{114\text{m}}\text{In}$  into 15 volume % HDEHP-n-heptane.

Fig. 4. Variations in  $1/K$  vs.  $\text{HCl}$  concentrations used as a back extractant for indium from solvent systems containing 15 volume % HDEHP-n-heptane.

Fig. 5. Gamma ray spectra of 2.81d  $^{111}\text{In}$  obtained on the 12M  $\text{HCl}$  back-extraction solution.













