

## Sequential Separation of $^{61}\text{Cu}$ , $^{62,63}\text{Zn}$ , $^{66,67,68}\text{Ga}$ , $^{71,72}\text{As}$ , and $^{73}\text{Se}$ Produced by Heavy Ion Activation on Cobalt Target

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A thick cobalt foil has been irradiated consecutively with  $^{16}\text{O}$ ,  $^7\text{Li}$ , and  $^{12}\text{C}$  beams to produce the 'tracer packet' containing carrier free radiotracers of Cu, Zn, Ga, Ge, As, and Se. The present work describes sequential separation of these product radionuclides by liquid-liquid extraction method.

### 1. Introduction

Recently, we have introduced the concept of "tracer packet" and developed radiochemical heavy ion activation method for the production of "tracer packet of micronutrient elements", e.g. Cu, Zn, Ga, Ge, As, and Se altogether by consecutive irradiation of a thick cobalt target with medium-energy  $^{16}\text{O}$ ,  $^7\text{Li}$ , and  $^{12}\text{C}$  projectiles followed by chemical separation of bulk cobalt from the carrier free products.<sup>1,2</sup> The importance of the production of tracer packet lies in the fact that the behaviour of all the micronutrient elements can be studied simultaneously in some definite physical, chemical or biological systems. However the use of multiple beam consecutively on a single target has another aspect, i.e., number of carrier free radionuclides are produced in a single target which reduces or minimizes the following: i) radiation hazard, ii) time required for handling of multiple targets, iii) chemical work up, etc.

All the essential elements discussed above have their own importance in biological systems and environment individually. For example, zinc plays an important role in many processes of metabolisms of living beings.  $^{65}\text{Zn}$  has been used in food for the zinc bioaccumulation study.<sup>3</sup> The contamination of arsenic, even in a minute scale in water or soil can cause serious impact on human health via the food chain. It is thus necessary to study the migration of arsenic either from ground water or from soil to the living systems. Radiotracer of arsenic would be more effective in studying the migration or presence of other elements in different media. Liquid waste arising from the processing of  $^{131}\text{I}$  contains significant quantities of  $^{75}\text{Se}$  ( $T_{1/2} = 119.7$  d) along with other radionuclides. The presence of this radionuclide necessitates the long-term storage of liquid waste prior to its disposal for the decay of  $^{75}\text{Se}$ . To minimize the storage time and to avoid consequences arising from prolong storage, a simple method for selective separation of selenium radionuclide is necessary. Moreover, selenium is also another important trace element in plant or animal metabolism.  $^{75}\text{Se}$  has been used to analyse the food quality in the Mediterranean crab *Pachygrapsus marmoratus*.<sup>4</sup>

Therefore, in the present work we have aimed to develop the radiochemical method for separation of individual elements contained in the tracer packet solution by liquid-liquid extraction (LLX).

### 2. Experimental

**2.1. Irradiation.** Cobalt foil of thickness  $17\text{ mg/cm}^2$  was

subjected to irradiation with a collimated beam of  $96\text{ MeV }^{16}\text{O}^{7+}$  at BARC-TIFR Pelletron, Mumbai, India, with an average beam current of  $300\text{ nA}$  for five hours. The total dose was  $4700\text{ }\mu\text{C}$ . Immediately after the irradiation with  $^{16}\text{O}$ , the projectile was switched to  $48\text{ MeV }^7\text{Li}^{3+}$  of  $100\text{ nA}$  beam current and the same target was irradiated for ten hours with a total dose  $8000\text{ }\mu\text{C}$ . The time required to change the beam and beam tuning was less than  $30\text{ min}$ . The same target was again irradiated (without removing the target from the irradiation chamber) with  $84\text{ MeV }^{12}\text{C}^{6+}$  of  $250\text{ nA}$  average beam current for two hours with a total dose  $1500\text{ }\mu\text{C}$ . The beam current was measured by a Faraday cup situated at the end of the target in conjunction with a current integrator. An electron suppresser was used to suppress the electrons at the Faraday cup.

The thick target was used with the idea that the incident beam will traverse through the target, losing its energy gradually, and at different degraded energy different nuclear reactions will be favored, resulting isotopes of different elements in the cobalt matrix. However, the thickness of the target was lower than that would be required for beam dumping, which was checked by the software TRIM<sup>5</sup> for all the projectiles. Terminal voltage ( $12\text{ MV}$ ) of the Pelletron was the deciding factor for choosing the projectile energy. The basis of choice in the beam sequence was that the longer half-life radionuclides should be produced first. For example, the products of  $\text{Co}(^{16}\text{O}, xn)$  reaction have longer half-lives than those of  $\text{Co}(^7\text{Li}, xn)$  or  $\text{Co}(^{12}\text{C}, xn)$  reaction. Similarly the products of  $\text{Co}(^7\text{Li}, xn)$  reaction have longer half-lives than those of  $\text{Co}(^{12}\text{C}, xn)$  reaction. After the third irradiation, cobalt target was removed from the irradiation chamber cooled for four hours and series of non-destructive gamma spectra were taken in regular interval. The corresponding photopeaks as well as decay profiles identified the product radionuclides.

An HPGe detector of  $2.13\text{ keV}$  resolution at  $1.33\text{ MeV}$  in conjunction with a PC based MCA, PCA2 (OXFORD), was used for  $\gamma$  spectrometric studies.

**2.2. Chemical Procedure.** The liquid cation exchanger, di-(2-ethylhexyl) phosphoric acid (HDEHP), the liquid anion exchanger, trioctylamine (TOA), and the neutral co-reagent, tributylphosphate (TBP), were procured from Merck. The extractant solution of desired concentrations was prepared by adding calculated amount of HDEHP, TBP or TOA to cyclohexane. After taking non-destructive spectra, the cobalt foil was dissolved in dilute  $\text{HNO}_3$ . In order to study the behavior of bulk cobalt radiometrically in the LLX system,  $^{60}\text{Co}$  was spiked at the time of dissolution. After dissolution of the cobalt foil the solution was evaporated to dryness and taken in  $0.1\text{ M HNO}_3$  medium.

In each step of the separation procedure, a few drops of the

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active stock solution were vigorously shaken with equal volume of the aqueous and organic solutions. The resulting solution was then allowed to settle and after the disengagement the separated phases were subjected to  $\gamma$  spectrometric studies.

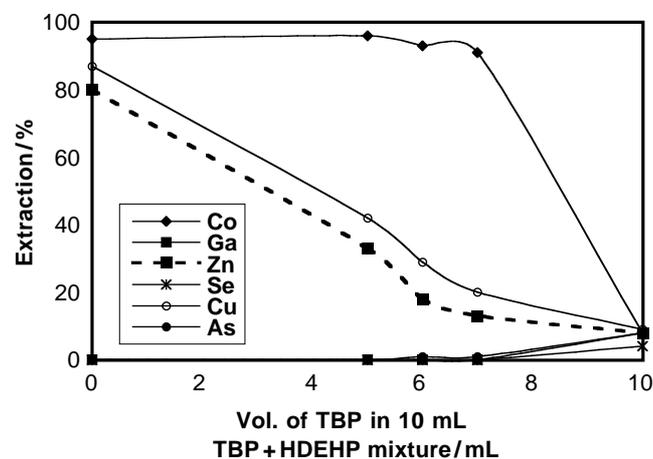
### 3. Results and Discussion

Nondestructive spectrum of  $^{16}\text{O}$ ,  $^7\text{Li}$ , and  $^{12}\text{C}$  activated cobalt target and analysis of decay pattern confirms the presence of  $^{61}\text{Cu}$ ,  $^{62,63}\text{Zn}$ ,  $^{66,67,68}\text{Ga}$ ,  $^{71,72}\text{As}$ , and  $^{73}\text{Se}$  in the matrix.

To remove bulk cobalt from the solution, extractions were carried out with varying concentrations of HDEHP and 25%  $\text{NH}_3$  solution. It was found that at 1% HDEHP concentration, the bulk cobalt was transferred into the organic phase quantitatively with some amount of carrier free  $^{61}\text{Cu}$  and  $^{62,63}\text{Zn}$ . The extraction of cobalt from the aqueous phase may be due to the formation of the cationic ammine complex, which was extracted by the cationic exchanger HDEHP. To prevent copper and zinc extraction TBP was mixed with HDEHP. Extractions with 1% HDEHP and 10% TBP mixture (v/v = 3:7) removed 92% bulk cobalt from the aqueous phase in a single run (Figure 1). Cu (20%) and Zn (13%) were also partly extracted with bulk cobalt in this condition. Extractions for three times in this condition removed almost all the bulk cobalt into the organic phase leaving the carrier free product radionuclides in the aqueous phase.

The ammoniacal solution containing  $^{61,62}\text{Cu}$ ,  $^{62,63}\text{Zn}$ ,  $^{66,67,68}\text{Ga}$ ,  $^{71,72}\text{As}$ , and  $^{73}\text{Se}$  was shaken with 5% HDEHP. In this condition,  $^{61,62}\text{Cu}$  and  $^{62,63}\text{Zn}$  were extracted into the organic phase leaving  $^{66,67,68}\text{Ga}$ ,  $^{71,72}\text{As}$ , and  $^{73}\text{Se}$  in the aqueous phase. This is due to the fact that copper and zinc form  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  and  $[\text{Zn}(\text{NH}_3)_4]^{2+}$ , respectively, which in turn were extracted by the organic reagent HDEHP. Cu and Zn were back-extracted using 1 M HCl as an aqueous solution. Then Zn was extracted by 0.1 M TOA keeping Cu in 1 M HCl solution. Extraction of Zn by TOA from HCl medium is attributed to the fact that in HCl medium zinc forms strong anionic complexes of the type  $[\text{ZnCl}_4]^{2-}$  which were taken up completely by the anionic exchanger (Separation factor,  $S_{\text{Zn}/\text{Cu}} = 1370$ ). Zinc was back-extracted using 0.1 M diethylenetriaminepentaacetic acid (DTPA) in 1 M NaOH.

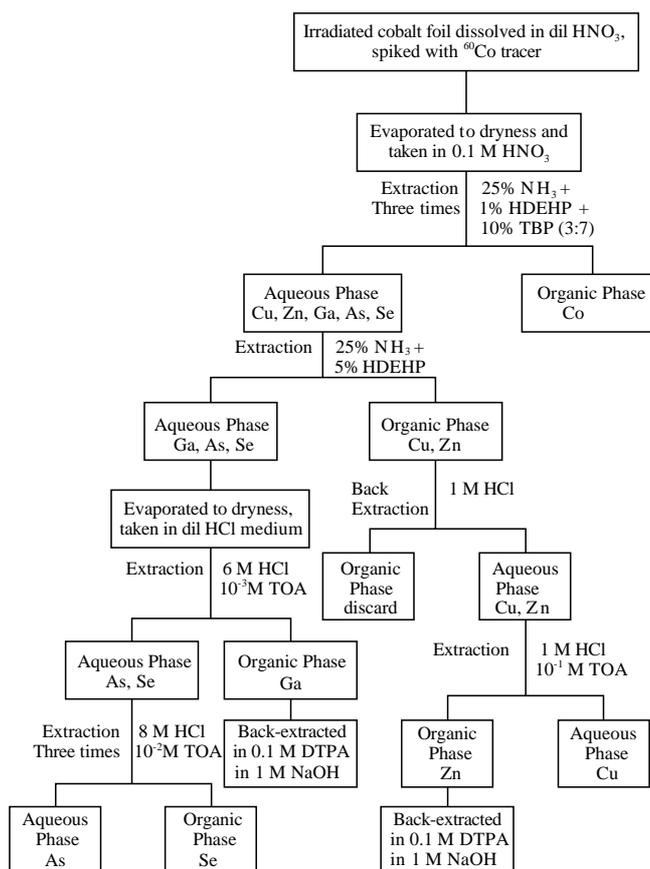
The ammoniacal solution containing Ga, As, and Se was evaporated to dryness to remove ammonia and then brought into HCl medium. Gallium was extracted in the organic phase at 6 M HCl and  $10^{-3}$  M TOA concentration.  $^{66,67,68}\text{Ga}$  radionuclides were transferred into the organic phase leaving As and Se completely in the aqueous phase ( $S_{\text{Ga}/\text{Se}} = 13000$ ,  $S_{\text{Ga}/\text{As}} = 648000$ ). The high extractability of carrier free gallium radionuclides in a HCl medium might be explained by the formation of  $[\text{GaCl}_4]^-$ , which in turn was extracted by the



**Figure 1.** Extraction profile of tracer packet and bulk cobalt with 25%  $\text{NH}_3$  and varying proportion of 1% HDEHP and 10% TBP (v/v).

anionic extractant TOA.<sup>6</sup> Extracted Ga was back extracted into the aqueous phase by using 0.1 M DTPA in 1 M NaOH. Separation of As from Se was achieved when extracted with  $10^{-2}$  M TOA and 8 M HCl. In this optimal condition, 60% of selenium was extracted in the organic phase keeping arsenic in the aqueous medium ( $S_{\text{Se}/\text{As}} = 600$ ). The reason might be due to the fact that at a particular HCl concentration Se preferably forms anionic complex  $[\text{SeCl}_6]^{2-}$  and is extracted by the anionic extractant TOA.<sup>7</sup> Distribution ratios at all optimal conditions have been tabulated in Table 1.

Schematically Figure 2 describes the sequential separation method of all these radionuclides.



**Figure 2.** Schematic diagram for the sequential separation of tracer packet of essential nutrient elements.

**Table 1: Distribution Ratios (D) of Co, Cu, Zn, Ga, As, and Se at Optimal Conditions**

Experimental Condition	$D_{\text{Co}}$	$D_{\text{Cu}}$	$D_{\text{Zn}}$	$D_{\text{Ga}}$	$D_{\text{As}}$	$D_{\text{Se}}$
25% $\text{NH}_3$ + 1% HDEHP + 10% TBP	10	0.24	0.14	$1.4 \times 10^{-4}$	0.008	$4.1 \times 10^{-4}$
25% $\text{NH}_3$ + 5% HDEHP	-	132.3	60	$2 \times 10^{-4}$	0.08	$5.7 \times 10^{-5}$
6 M HCl + $10^{-3}$ M TOA	-	-	-	386	$6 \times 10^{-4}$	0.03
8 M HCl + $10^{-2}$ M TOA	-	-	-	-	$1.3 \times 10^{-3}$	0.81
1 M HCl + $10^{-1}$ M TOA	-	0.07	100	-	-	-

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