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# REACTOR NEUTRON CROSS SECTIONS FOR PRODUCTION OF PHOSPHORUS-33 FROM CHLORINE-36 AND ENRICHED SULFUR-33 IN THE OAK RIDGE RESEARCH REACTOR

R. E. Lewis
T. A. Butler

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# REACTOR NEUTRON CROSS SECTIONS FOR PRODUCTION OF PHOSPHORUS-33 FROM CHLORINE-36 AND ENRICHED SULFUR-33 IN THE OAK RIDGE RESEARCH REACTOR

R. E. Lewis and T. A. Butler

## ABSTRACT

Enriched $^{33}S$, prepared by electromagnetic separation techniques, and $^{36}Cl$, prepared by reactor irradiation of natural chlorine, were evaluated as targets for the production of $^{33}P$ by the $^{33}S(n,p)^{33}P$ and $^{36}Cl(n,\alpha)^{33}P$ reactions. The reactor neutron cross sections of these reactions and those of the $^{32}S(n,p)^{32}P$ and $^{35}Cl(n,\alpha)^{32}P$ reactions were measured in positions 1.5, 3.3, 5.0, and 33 cm from the fuel element in the Oak Ridge Research Reactor (ORR). The reactor neutron cross sections of the $^{33}S(n,p)^{33}P$ and $^{36}Cl(n,\alpha)^{33}P$ reactions were relatively higher than those of the $^{32}S(n,p)^{32}P$ and $^{35}Cl(n,\alpha)^{32}P$ reactions with increasing distance from the fuel elements. Using target material containing mixtures of $^{33}S$ with $^{32}S$ and $^{36}Cl$ with $^{35}Cl$, it was necessary to age the $^{32,33}P$ mixture several months to prepare $^{33}P$ containing $<5\%$ $^{32}P$.

The ORR position for irradiation of sulfur enriched in $^{33}S$, which gave the highest yield of $^{33}P$ containing 5% $^{32}P$ after several months' aging, was ~5 cm from the fuel element. In this position, the reactor cross section of the $^{33}S(n,p)^{33}P$ reaction was 11.3 mb, and of the $^{32}S(n,p)^{32}P$ reaction was 9.2 mb.

The reactor position for irradiation of chlorine enriched in $^{36}Cl$ which gave the highest yield of 95% $^{33}P$ after aging several months was ~3.3 cm from the fuel element. In this position the reactor neutron cross section of the $^{36}Cl(n,\alpha)^{33}P$ reaction was 13.2 mb, and of the $^{35}Cl(n,\alpha)^{32}P$ reaction was 10.2 mb.

Procedures for the separation and recovery of carrier-free $^{32,33}P$ from elemental sulfur and KCl are described.

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## INTRODUCTION

The availability of millicurie quantities of $^{33}P$ would open many opportunities for research, especially in the biochemical sciences. In comparison to $^{32}P$, $^{33}P$ has a longer half-life (25 days as compared to 14.3 days), a lower maximum beta energy (~0.25 Mev as compared to ~1.7 Mev), and consequently less bremsstrahlung production. Specific uses for which this radioisotope could be used advantageously include autoradiography,[1] study of relative effects of recoil energy of sulfur produced by decay of $^{32}$P and $^{33}$P, long-term ecological and agricultural studies, synthesis of tagged complex organophosphorus compounds, and double labeling of phosphorus in complex molecules such as nucleic acids. More detailed reviews on specific uses have been given elsewhere.[2,3]

A long-lived $^{33}$P isotope was predicted and the existence of this isotope was confirmed in 1951 by Sheline.[2] Half-life and maximum beta energy measurements of this beta emitter are reviewed in Table 1.

Table 1. Half-life and maximum beta energy of $^{33}$P (Ref. 2,4-9)

| Half-life, days | Maximum beta energy, Mev | Reference[a] |
|---|---|---|
| 25.0 ± 2.0 | 0.26 ± 0.010 | 2, 1951 |
| 24.8 ± 0.5 | 0.26 ± 0.010 | 4, 1952 |
| 25.0 ± 2.0 | 0.25 ± 0.005 | 5, 1952 |
| 25.4 ± 0.2 | 0.249 ± 0.002 | 6, 1954 |
| 24.4 ± 0.2 | - | 7, 1954 |
| - | 0.252 ± 0.005 | 8, 1954 |
| 25.2 ± 0.5 | - | 9, 1960 |

[a] The reader is referred to the original articles for the meaning of the precision quoted.

Phosphorus-33 has been prepared in small quantities from thermal neutron irradiation of natural sulfur[3,5,10,11] by the $^{33}$S(n,p)$^{33}$P reaction, by charged-particle bombardment[12] to produce $^{33}$P by the $^{30}$Si($\alpha$,p)$^{33}$P reaction, by the photodisintegration reactions[2] $^{34}$S($\gamma$,p)$^{33}$P, $^{35}$Cl($\gamma$,2p)$^{33}$P, and $^{37}$Cl($\gamma$,$\alpha$)$^{33}$P, and by the $^{31}$P(t,p)$^{33}$P reaction.[13] Yields were too low in most cases to be practical for production of $^{33}$P.

In the present work, enriched $^{33}$S and $^{36}$Cl were evaluated as target materials for the production of $^{33}$P. This report describes the reactor neutron cross section measurements of the $^{33}$S(n,p)$^{33}$P, $^{32}$S(n,p)$^{32}$P, $^{36}$Cl(n,$\alpha$)$^{33}$P, and $^{35}$Cl(n,$\alpha$)$^{32}$P reactions in positions of various distances from the reactor fuel element. Also, chemical procedures for recovery and purification of the carrier-free phosphorus activities are described.

## MATERIALS AND METHODS

### Target Material

Duplicate samples of enriched $^{33}$S and $^{36}$Cl were irradiated in various positions of the ORR.

The sulfur target material was enriched in $^{33}$S by electromagnetic separation of the sulfur isotopes. Its isotopic mass composition at the 95% confidence level was as follows:

| | |
|---|---|
| $^{32}$S | 84.6 ± 0.05% |
| $^{33}$S | 11.56 ± 0.05% |
| $^{34}$S | 3.77 ± 0.05% |
| $^{36}$S | $\leq$0.05 |

Samples of 8-10 mg elemental sulfur were weighed to ± 0.05 mg and encapsulated in quartz for irradiation.

The chlorine target material was obtained from a target of natural chlorine which had been irradiated in the ORR at a neutron flux of ~$2.5 \times 10^{14}$ n/cm$^2$.sec for about four years to form $^{36}$Cl by the $^{35}$Cl(n,$\gamma$)$^{36}$Cl reaction. The chlorine was separated from the $^{35}$S and $^{32,33}$P activities by passing an aqueous solution of the NaCl target through a column of hydrous zirconium oxide (Bio-Rad HZO-1). The isotopic mass composition of the chlorine at the 95% confidence level was as follows:

| | |
|---|---|
| $^{35}$Cl | 38.17 ± 0.10% |
| $^{36}$Cl | 37.53 ± 0.10% |
| $^{37}$Cl | 24.20 ± 0.10% |

Samples of 100 mg NaCl were weighed to ± 0.05 mg and encapsulated in quartz for irradiation.

### Irradiation Facilities

Four reactor positions in the Oak Ridge Research Reactor (ORR)[14,15] were used in this study to determine the effect of the distance of the target material from the fuel element on the reactor neutron cross sections of the four reactions. These positions are described in Table 2.

Table 2. ORR positions and characteristics

| Position | Sample distance from nearest fuel element, cm | $\phi_{th}$, n/cm$^2$.sec | $\frac{\phi_f}{\phi_{th}}$ |
|---|---|---|---|
| Hydraulic tube No. 11 | ~ 1.5 | $2 \times 10^{14}$ | 0.45 - 0.56 |
| NF stringer | ~ 3.3 | $2.5 \times 10^{14}$ | 0.37 - 0.43 |
| Isotope stringer No. 1 | ~ 5.0 | $2 \times 10^{14}$ | 0.18 - 0.23 |
| Water irradiation facility | ~ 33.0 | $2 \times 10^{12}$ | 0.035 - 0.05 |

The thermal neutron flux was measured by the $^{59}$Co(n,$\gamma$)$^{60}$Co reaction (37 b),[16] and the fast neutron flux by the $^{54}$Fe(n,p)$^{54}$Mn reaction (60 mb).[17]

## Recovery of $^{32,33}$P for Reactor Neutron Cross Section Determination

Tracer studies with $^{32}$P showed phosphorus as phosphate could be quantitatively separated from other activities by extracting the $^{32}$P into n-butanol as phosphomolybdic acid. This procedure was not useful as a production method of recovering $^{32,33}$P because of the difficulty in separating phosphorus and molybdenum; however, it was useful for quantitatively separating millicurie amounts of $^{32,33}$P from curie quantities of $^{35}$S for determining reactor neutron cross sections.

The sample was acidified with $H_2SO_4$ and HCl to 0.5 M in each. The solution was made 1 g/liter molybdic acid, heated for ~5 min, and cooled to room temperature. Phosphomolybdic acid was then extracted with n-butyl alcohol.

The $^{32,33}$P was recovered from enriched sulfur by dissolving the sulfur sample in dichloroethylene and extracting the phosphorus activity with hot 0.1 N HCl.

## Identification of $^{33}$P

The $^{32}$P and $^{33}$P were assayed by beta liquid scintillation spectrometry by use of $^{32}$P and $^{45}$Ca as calibration standards.

The weak beta emitter was identified as $^{33}$P by comparing the $^{32}$P/$^{33}$P ratio before and after several chemical procedures. There was no change in the ratio after precipitation of $MgNH_4PO_4$, extraction of phosphomolybdate, precipitation of $CaSO_4$ from acidic solution, and coprecipitation of the phosphate with $MgNH_4AsO_4$. Removal of $AsO_4^{3-}$ by evaporation with HBr did not change the $^{32}P/^{33}P$ ratio. These procedures indicated the low-energy beta emitter was not $^{45}Ca$, $^{35}S$, or As activities. Feather-plot analysis and half-life measurements indicated the beta energy was ~0.25 Mev and the half-life was about 25 days, confirming the activity as $^{33}P$.

Reactor Neutron Cross Sections

The values for the (n,p) and (n,$\alpha$) cross sections, expressed as reactor neutron cross sections, $\sigma_{reactor}$, were calculated in the following manner. From the disintegration rate at the end of the irradiation (dn/dt), the rate of the reaction R was calculated by the equation

$$R = \frac{dn/dt}{N_o(1-e^{-\lambda t})} ,$$

where

$N_o$ = number of atoms of target nuclides
$\lambda$ = disintegration constant of the reaction product
t = time of irradiation.

The reactor neutron cross section was obtained by

$$\sigma_{reactor} = \frac{R}{nv_o} .$$

The thermal flux, $nv_o$, was measured with a cobalt monitor in the irradiation can. The reactor neutron cross sections are useful for calculating yields of $^{32}P$ and $^{33}P$ in specific positions of the ORR.

## RESULTS AND DISCUSSION

Reactor neutron cross sections of $^{32}S(n,p)^{32}P$ and $^{33}S(n,p)^{33}P$ reactions increased with decreasing distance from the fuel element. The $^{32}S(n,p)^{32}P$ reactor neutron cross section was considerably higher than the $^{33}S(n,p)^{33}P$ reactor neutron cross section in positions near the fuel element; however, the ratio of the $^{33}S(n,p)^{33}P$ to $^{32}S(n,p)^{32}P$ reactor neutron cross sections increased with increasing distance from the fuel element. The reactor neutron cross sections of the two reactions at various distances from the fuel element are shown in Table 3.

Table 3. Reactor neutron cross sections of the $^{32}S(n,p)^{32}P$ and $^{33}S(n,p)^{33}P$ reactions

| Sample distance from fuel element, cm | $\sigma_{reactor}$, mb | | |
|---|---|---|---|
| | $^{32}S(n,p)^{32}P$ | $^{33}S(n,p)^{33}P$ | $\sigma^{33}P:\sigma^{32}P$ |
| 1.5 | 59.8 | 22.0 | 0.37 |
| 3.3 | 27.7 | 19.0 | 0.68 |
| 5.0 | 9.2 | 11.3 | 1.23 |
| 33.0 | 1.5 | 3.7 | 2.38 |

## Reactor Neutron Cross Sections of $^{35}Cl(n,\alpha)^{32}P$ and $^{36}Cl(n,\alpha)^{33}P$ Reactions

The reactor neutron cross sections of the $^{35}Cl(n,\alpha)^{32}P$ and $^{36}Cl(n,\alpha)^{33}P$ reactions also increased with decreasing distance from the fuel element but not as greatly as those for sulfur. The ratio of the reactor neutron cross section of the $^{36}Cl(n,\alpha)^{33}P$ reaction to the $^{35}Cl(n,\alpha)^{32}P$ reaction increased with increasing distance from the fuel element (Table 4).

Table 4. Reactor Neutron Cross Sections of the $^{35}Cl(n,\alpha)^{32}P$ and $^{36}Cl(n,\alpha)^{33}P$ reactions

| Sample distance from fuel element, cm | $\sigma_{reactor}$, mb | | |
|---|---|---|---|
| | $^{35}Cl(n,\alpha)^{32}P$ | $^{36}Cl(n,\alpha)^{33}P$ | $\sigma^{33}P:\sigma^{32}P$ |
| 1.5 | 7.25 | 8.2 | 1.20 |
| 3.3 | 10.2 | 13.2 | 1.30 |
| 5.0 | 5.8 | 9.5 | 1.64 |
| 33.0 | 1.3 | 2.4 | 1.89 |

The higher ratio of the reactor neutron cross sections producing $^{33}P$ to those producing $^{32}P$ at positions of increasing distances from the fuel element indicated that positions further away from the fuel elements were more favorable for production of $^{33}P$ low in $^{32}P$ from $^{33}S$ (Table 3) or $^{36}Cl$ (Table 4). The relatively greater decrease in the reactor neutron cross sections of the $^{32}S(n,p)^{32}P$ and $^{35}Cl(n,\alpha)^{32}P$ as compared to the reactor neutron cross sections of the $^{33}S(n,p)^{33}P$ and $^{36}Cl(n,\alpha)^{33}P$ may be due to distortions of the fission neutron spectrum as the neutrons pass through the water moderator. Recent experiments[18-20] have shown that the fission neutron spectrum in water is depleted in 2.5-4 Mev neutrons with respect to neutrons of higher energies.

## Production of $^{33}P$ in the ORR

The yield of $^{32}P$ and $^{33}P$ at reactor discharge time depends on the percentages of target isotopes, reactor neutron cross sections, neutron flux, and irradiation time.

The best of the four ORR positions studied for production of $^{33}P$ from $^{33}S$ by fast-neutron irradiation was the Isotope Stringer No. 1. In this position, the sample was located in the highest flux ~5 cm from the fuel element. The thermal-neutron flux was 2.0-2.5 x $10^{14}$ n/cm$^2$.sec and the reactor neutron cross sections of the $^{33}S(n,p)^{33}P$ and $^{32}S(n,p)^{32}P$ reactions were 11.3 mb and 9.2 mb, respectively. With present isotope separation techniques, the enriched $^{33}S$ has been limited to milligram quantities[21] of ~70% product.

The best ORR position of the four positions studied for production of $^{33}P$ from $^{36}Cl$ by the $^{36}Cl(n,\alpha)^{33}P$ reaction was the midregion of the NF stringer. The sample was located ~3.3 cm from the fuel element and the thermal flux was 2.5-3.0 x $10^{14}$ n/cm$^2$.sec. The reactor neutron cross sections of the $^{36}Cl(n,\alpha)^{33}P$ and $^{35}Cl(n,\alpha)^{32}P$ reactions were 13.2 mb and 10.2 mb, respectively. Chlorine-36 has been prepared in gram quantities with 38% $^{36}Cl$ (~37% $^{35}Cl$).

The $^{33}P$ produced by both methods contains appreciable quantities of $^{32}P$ which must be removed by aging the $^{32,33}P$ mixture. The aging period depends on the $^{33}P/^{32}P$ ratio and the percentage of $^{32}P$ that can be tolerated in the final product.

As higher enrichments of $^{33}S$ and $^{36}Cl$ become available, yields of >95% $^{33}P$ will be considerably higher because the aging period required to reduce the $^{32}P$ content will be shorter, and consequently the yield of $^{33}P$ greater.

## Production Method of Recovery and Purification of $^{32,33}$P

The $^{33}$P must be carrier free to be of greatest use in biochemical studies. Also, $^{33}$P must be free of other radioisotopes, such as $^{35}$S and $^{36}$Cl. The following procedures were developed for recovery of carrier-free $^{33}$P.

Phosphorus-32 and $^{33}$P from Enriched $^{33}$S. Neutron irradiation damages the structure of sulfur, forming $S_{\mu}$, a carbon disulfide-insoluble form of amorphous sulfur. Before the phosphorus activities could be leached from this sulfur, it was converted to rhombic sulfur by heating[22] for 16 hr at 108°C. The sulfur was then dissolved in carbon disulfide and extracted[23] with an equal volume of 1 M HCl. Heating the solutions to reflux temperature aided in the removal of the phosphorus activities. The aqueous phase, which contained the phosphorus activities, was evaporated to a low volume and diluted with distilled water to ~0.1 M HCl. The $^{32,33}$P mixture was then aged 3-4 months until the $^{32}$P content was $\leq$5% of the $^{33}$P content.

Sulfur was recovered for further irradiation by evaporating the sulfur-carbon disulfide solution to dryness.

Phosphorus-32 and $^{33}$P from $K^{36}Cl$ Target. The $K^{36}Cl$ was dissolved in water and passed through a 3-ml bed of Bio-Rad HZO-1, a hydrous zirconium oxide at pH 8. The $^{32,33}$P and $^{35}$S activities were retained on the column while the KCl was not sorbed. Sulfur-35 was then eluted with 100 ml of 0.5 M $NH_4OH$, and $^{32,33}$P recovered by elution with 30 ml of 6 M KOH at 70°C. After the KOH was neutralized with HCl, the KCl solution was passed through a $H^+$-form Dowex 50-8X column to remove $K^+$, the effluent containing the $^{32,33}$P evaporated to a low volume and diluted to ~0.1 M HCl. The $^{32,33}$P mixture was then aged until the $^{32}$P content was $\leq$5% of the $^{33}$P.

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