

Studies of Preparation of
Phosphorus - 32

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Abstract

^{32}P is easily and quantitatively separated from the bulk of sulphur target by shaking carbon disulfide solution of neutron irradiated sulphur with dilute ammonia. Extraction with acid solution gives a lower recovery.

Although bromoform is another solvent for sulphur, low solubility of sulphur in it is not preferable.

From the aqueous extract, ^{32}P is purified by either ion-exchange or solvent extraction. In the ion-exchange method ^{32}P adsorbed on an anion-exchanger column (Daiiaion SA100) as orthophosphate is eluted with 0.05N hydrochloric acid. Initial small fraction of the eluate is taken as the product. Preliminary removal of the impurity by cation exchange is recommended in order to process a large quantity of sulphur.

In the solvent extraction method, the acidified extract is shaken twice with butyl acetate after addition of a small quantity of ammonium molybdate. ^{32}P is extracted back with water.

For the processing of ^{32}P the ion-exchange method is more convenient than the solvent extraction method.

According to the carbon disulfide-ammonia extraction followed by ion-exchange purification, the product of ^{32}P was obtained with a recovery of 92%. The radiochemical purity was high.

As carbon disulfide is inflammable, the following procedures are recommended for safe operation:

- (1) Used carbon disulfide is removed immediately, and is kept under a water layer after diluted with carbon tetrachloride.
- (2) A closed hood is used and the nitrogen jet is prepared for fire.

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リン - 32 の 製 造 研 究

要 旨

中性子を照射したイオウの CS_2 溶液を希アンモニア水と振りまぜると、多量のイオウターゲットから容易に定量的に ^{32}P が分離される。酸溶液による抽出では収率が低い。

イオウの溶媒としてプロモフォルムもあるが、イオウの溶解度が小さいので適当でない。

抽出液から ^{32}P をイオン交換法、または溶媒抽出法により精製する。イオン交換法では、 ^{32}P を正リン酸として陰イオン交換樹脂(ダイイオン SA100)に吸着させ、0.05 N HCl で溶離し、溶離液の最初の部分のみをとって製品とする。多量のイオウを処理する場合には、あらかじめ陽イオン交換樹脂により不純物を除く必要がある。溶媒抽出法では少量のモリブデン酸アンモニウムを加え、抽出液を酸性にして酢酸ブチルで2回抽出する。そして ^{32}P を水で逆抽出する。 ^{32}P の精製法としては、イオン交換法が抽出法よりすぐれている。 CS_2 -アンモニア抽出ののち、イオン交換精製を行なうと、 ^{32}P の収率は92%で、放射化学的純度は良好であった。

CS_2 は可燃性であるので、安全のため次の処置が必要である。

- ① 使用済み CS_2 をただちに取り除き、 CCl_4 で希釈後、水層下におく。
- ② 気密フードを用い、火災にそなえ、 N_2 ガスの吹き込み口をつける。

昭和35年10月

日 本 原 子 力 研 究 所

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References

Introduction

According to the programme of the Japan Atomic Energy Research Institute, ^{32}P , one of the most common radionuclides with a short half-life, is supposed to be produced in a multi-curie scale with JRR-2 or 3 which will be operated soon.

In order to contribute toward this programme, the present authors studied the chemical process for the isolation of ^{32}P formed by (n,p)-reaction in a large amount of irradiated sulphur target.

After discussing many known processes, (1), (2), (3), (4), and (5) for ^{32}P , the old solvent extraction method (6) was taken and modernized. In the present method, all treatments can be carried out under atmospheric pressure and at below 100°C keeping most of the active material in a solution throughout the whole processing.

Commercial sulphur of analytical grade, is used as a target without any purification.

Carbon disulfide and bromoform are taken as the solvent for irradiated sulphur. Although the solubility of sulphur in carbon disulfide is higher than that in bromoform, carbon disulfide is much more inflammable than bromoform is.

In the present study, ^{32}P is usually extracted from a carbon disulfide solution of the irradiated target. Fire is avoided by the following precautions:

(1) Carbon disulfide is transferred under water layer immediately after use, removed from the production apparatus, and diluted with carbon tetrachloride.

(2) Ventilation of high degree.

(3) For emergency use nitrogen jet devices are equipped inside of the box which contains the apparatus.

From the organic solution almost 100% ^{32}P is recovered by shaking with dilute ammonia. ^{32}P thus obtained is purified by an ion-exchange method.

Thus, the solvent extraction method which has not been used for the routine work is promised a revival.

1. Isolation of P-32 from Large Amounts of Irradiated Sulphur.

An organic solution of irradiated sulphur (10g S/l) was shaken with various aqueous solutions in order to check the distribution of ^{32}P radiometrically. The volume ratio was kept (5 ml: 5 ml). 50% carbon disulfide in benzene, undiluted carbon disulfide and bromoform were taken as organic solvents for sulphur. The results obtained are summarized in Table 1.

Table 1. Extraction of ^{32}P from irradiated sulphur

<u>Organic layer</u>	<u>Aqueous layer</u>	<u>Extraction yield in aq. layer</u>
S in 100% CS_2	1N NH_4OH	94%
	2N "	95
	3N "	99
S in 50% CS_2	1N NH_4OH	96
	2N "	99
	3N "	99
	4N "	99
	1N HNO_3	71
	2N "	70
	3N "	64
	4N "	64
S in 100% CHBr_3	1.5N NH_4OH	84
	3N "	72
	4.5N "	78
	6N "	80
	7N "	83
	1N HCl	43
	2N "	42
	4N "	41
	6N "	41
	1N HNO_3	60
	2N "	60
	3N "	62
	4N "	61
	5N "	64

Errors in the extraction given in Table 1 are estimated to be about several per cent.

1-4N ammonia extracts almost all ^{32}P from carbon disulfide solutions of sulphur, whereas 1-4N nitric acid extracts about 65-70% ^{32}P . From bromoform solution 1.5-7N ammonia, 1-8N hydrochloric acid and 1-5N nitric acid recover around 80, 40 and 60% ^{32}P respectively. In any case, sulphur remains in the organic phase almost completely.

Many portions of an organic solution of irradiated sulphur were shaken with the same portion of aqueous ammonia successively. As is seen in Table 2, the distribution of ^{32}P is kept practically constant through 1st-4th or 5th contracts.

This shows that ^{32}P can be concentrated in a small volume of aqueous ammonia from a large volume of the organic solution of sulphur by the successive extraction.

Table 2. Repeated extraction with the same aqueous solution

No. of extraction		1	2	3	4	5	6
Extraction yield of ^{32}P	A	92	98	99	99	-	-
	B	98	98	94	95	88	87
	C	86	97	99	93	90	-
	D	56	53	57	50	53	-

(Note)

- A: organic phase, S in 100% CS_2 , 130g S/l CS_2 ,
aqueous phase, 2N NH_4OH ,
volume ratio, org. 5ml/aq. 5ml.
- B: organic phase, S in 100% CS_2 , 400g S/l CS_2 ,
aqueous phase, 3N NH_4OH ,
volume ratio, org. 500ml/aq. 200ml.
- C: organic phase; S in 100% CHBr_3 , 40g S/l CHBr_3 ,
aqueous phase, 2N NH_4OH ,
volume ratio, org. 10ml/aq. 10ml.
- D: organic phase; S in 100% CHBr_3 , 40g S/l CHBr_3 ,
aqueous phase, 2N HNO_3 ,
volume ratio, org. 5ml/aq. 5ml.

Usually the direct extraction of ^{32}P with an acid solution is not successful. After irradiated sulphur suspension in the mixture of concentrated and fuming nitric acid is dissolved off with carbon disulfide, ^{32}P remains in the acid solution.

Based on the results mentioned above, it is concluded that the ammonia extraction is the most suitable for separating ^{32}P from the bulk of irradiated sulphur. In the present work carbon disulfide was used hereafter as the solvent for sulphur. Processes with bromoform will be written elsewhere.

2. Radiochemical Purification of P-32

Both solvent extraction and ion exchange methods are studied in order to find out a nice process for the purification of ^{32}P .

2.1 Solvent Extraction Method

^{32}P is quantitatively extracted with butylacetate from about 0.5N hydrochloric acid solution after adding a small amount of ammonium molybdate (7). In this case, it is believed that the organic solvent extracts carrier-free ^{32}P as phosphomolybdate.

Scrubbing the organic extract with water brings about an aqueous solution of ^{32}P very easily. As far as ^{32}P is carrier-free, the resultant aqueous solution does not contain a noticeable amount of molybdate. However, the very small amounts of molybdate can be removed by shaking the aqueous solution with TBP after adjusting the acidity of the aqueous solution 2N in hydrochloric acid.

The distribution ratios between 2N hydrochloric acid and undiluted TBP are ~ 10 for molybdate and ~ 0.3 for phosphate respectively(8).

Experimental data are given in the following part.

2.2 Ion Exchange Method

2.2.1 Mutual separation of phosphate and sulfate: A sulfate is the most predominant impurity to be eliminated, ^{32}P is purified from sulfate with a Diaion SA100 column (10mm ϕ , 86mm long). Diaion SA100 is an anion exchanger and is used in 100-200 mesh fine powder after conditioning with hydrochloric acid. Both phosphate and sulfate are adsorbed on the resin from very diluted acid solution. 0.01N hydrochloric acid brings about the elution curves for phosphate and sulfate as is shown in Fig. 1, and similar results of elution with 0.05N hydrochloric acid are shown in Fig. 2. Figs. 1 and 2 show that the separation with 0.05N hydrochloric acid is preferable because of following reasons:

In elution with 0.05N hydrochloric acid, most of the ^{32}P is found in the first 15ml portion. This portion of the eluate is easily collected without any monitoring of activity. On the other hand, elution with 0.01N hydrochloric acid results in about 50ml solution of purified ^{32}P , and the collection of that portion might need a radioactivity surveying. Adsorption of ^{32}P on vessel walls is supposed to be reduced in a solution of higher acidity.

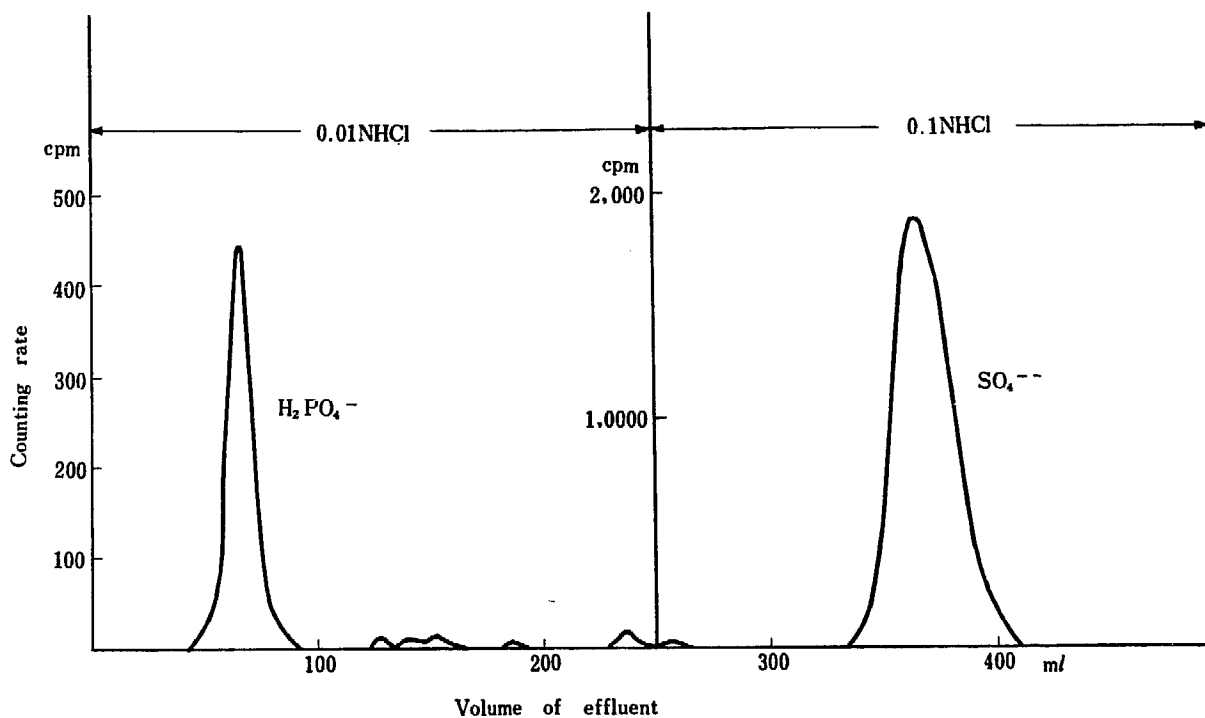


FIG. 1 Elution curves of $H_2PO_4^-$ and SO_4^{--} Diaion SA100, 100 ~ 200 mesh, 10mm ϕ x 86mm, flow rate 1.2ml/min.

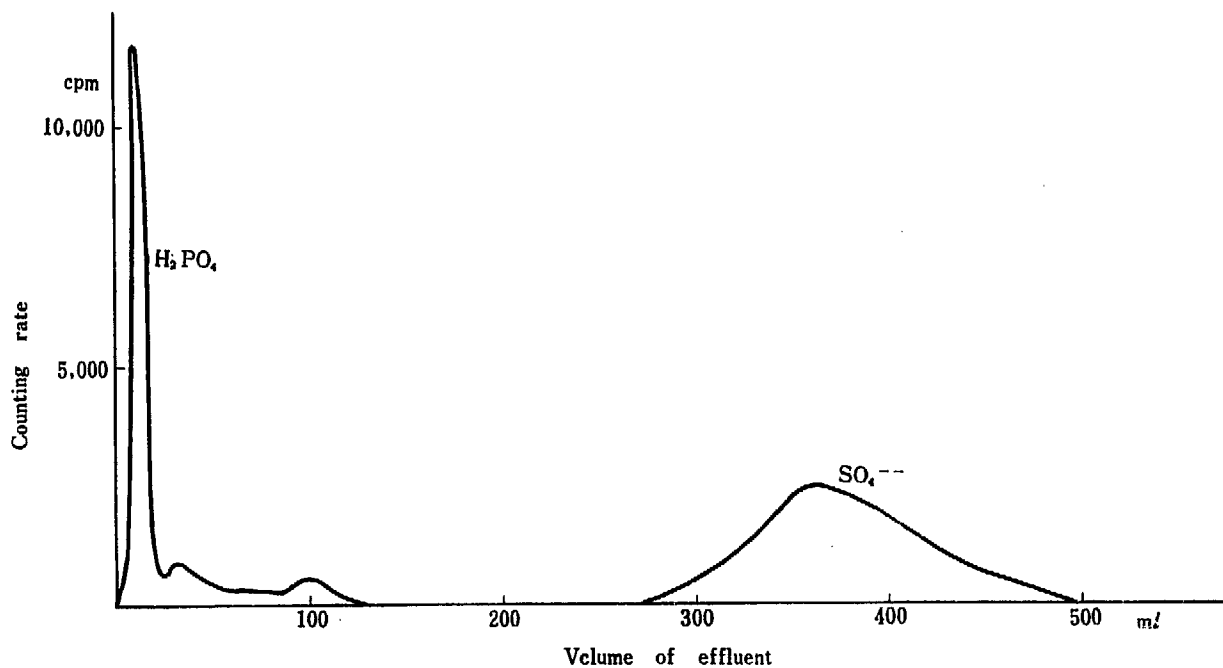


FIG. 2 Separation of $H_2PO_4^-$ from SO_4^{--} Elution with 0.05N hydrochloric acid. Diaion SA100, 100 ~ 200 mesh, 10mm ϕ x 86mm, flow rate 1.2ml/min.

2.2.2 Pretreatment: The ammonium hydroxide extract obtained by (1) is dried up. More than 95% of the ^{32}P is easily taken up by dissolving the residue with 16N nitric acid, 6N hydrochloric acid or distilled water. However, hydrochloric acid is not able to bring about a clear solution as it can not oxidize sulfide or sulphur component of the residue, whereas dissolution with water lowers the recovery of ^{32}P sometimes because of high adsorption of ^{32}P on undissolved particles or the vessel walls.

Nitric acid results in a clean solution of the residue, decomposing sulfide component very well and coagulating sulphur particles. The recovery of ^{32}P in nitric acid dissolution is kept high independently of the amount of sulphur target (100 - 1,000g) or the residue of the ammonia extract.

On the other hand, it is found that the anion-exchange separation mentioned above is interfered with the amount of cations in the solution and ^{32}P tends to pass through the column. Therefore the removal of cations with a cation exchange of phosphate and sulfate is desired.

Based on these reasons, the following treatment is recommended between processes discussed in 1 and 2.1:

The residue of ammonium hydroxide extract is dissolved with a small volume of concentrated nitric acid. The resultant solution is evaporated again and converted into a very dilute hydrochloric acid solution. The cations which come from the impurity of the target are removed by passing through a cation exchange resin column (Diaion SK 1, 100-200 mesh, 10mm ϕ x 100mm).

The hydrochloric acid solution passed the column is evaporated and the residue is dissolved in distilled water. The almost neutral solution is passed through the anion-exchange column in order to make both phosphate and sulfate adsorbed on the resin. Active phosphate is eluted with a small volume of 0.05N hydrochloric acid as described above leaving sulfate on the resin. After sulfate remained is washed out by further elution with the acid, the resin column can be used again.

3. Flow Sheets

100-1,000g sulphur targets irradiated in JRR-1 for 15 - 30 hours were treated according to the three kinds of flow sheets which consist of the combination of the chemical treatments separately discussed above. Although the targets were irradiated with the neutron-flux of 10^{11} n/cm 2 /sec, different amounts were formed according to the differences in geometrical conditions of the irradiation or operational conditions of the nuclear reactor. For the experiments described below no remote-control devices were used as the amount of ^{32}P was less than a few mc.

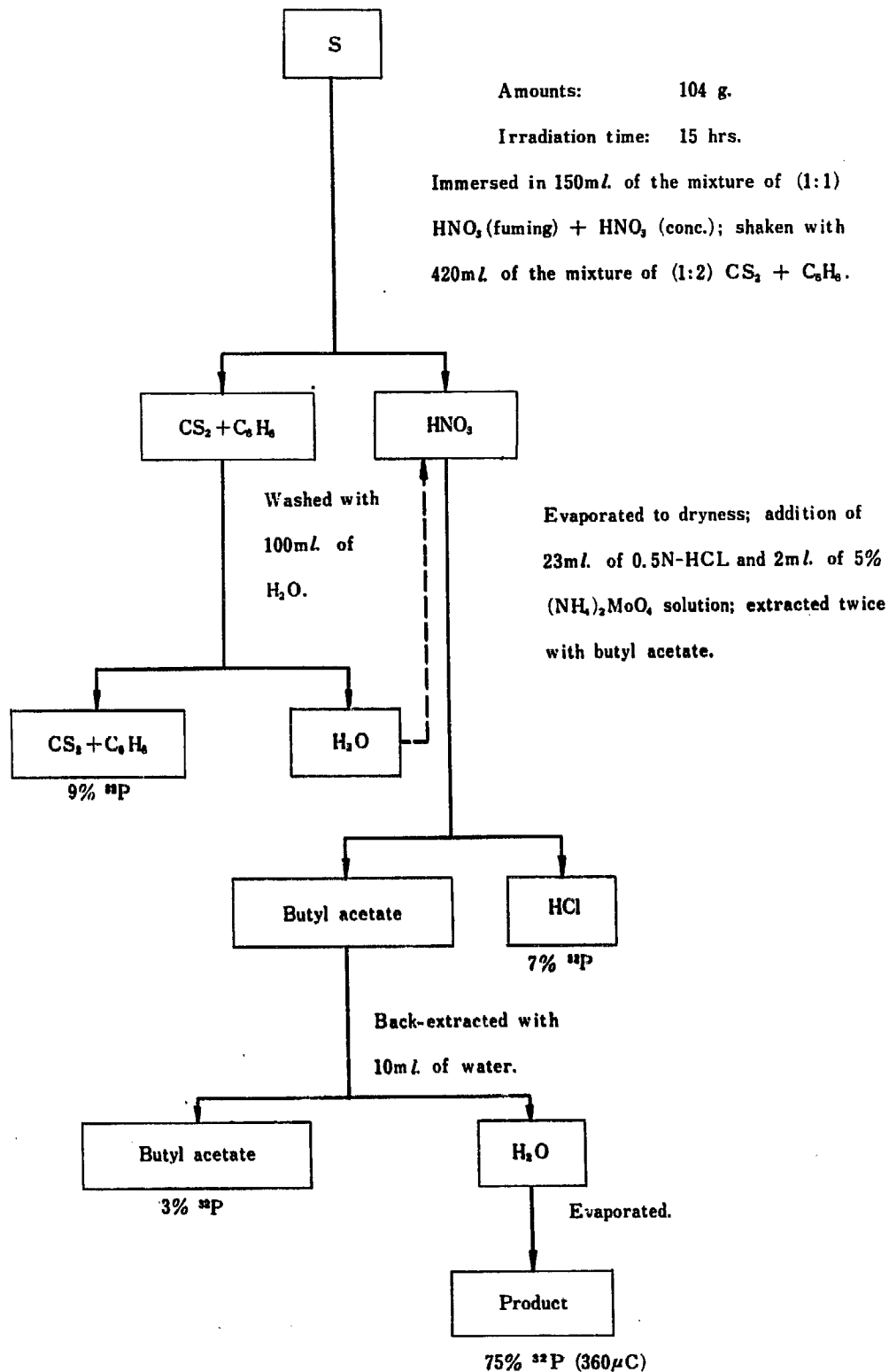


FIG. 3 Flow sheet for the nitric acid process.

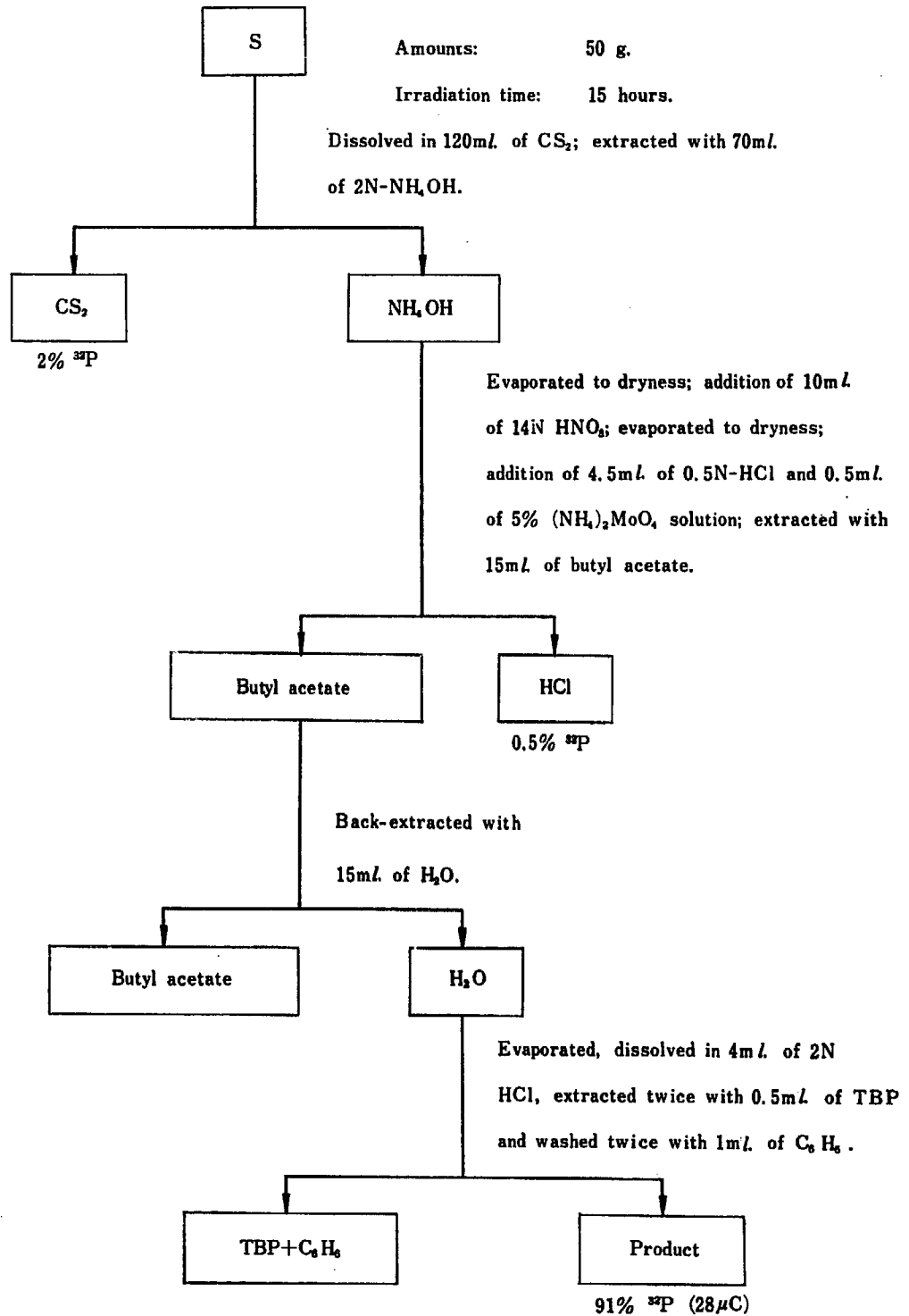


FIG. 4 Flow sheet for the ammonia-solvent extraction process.

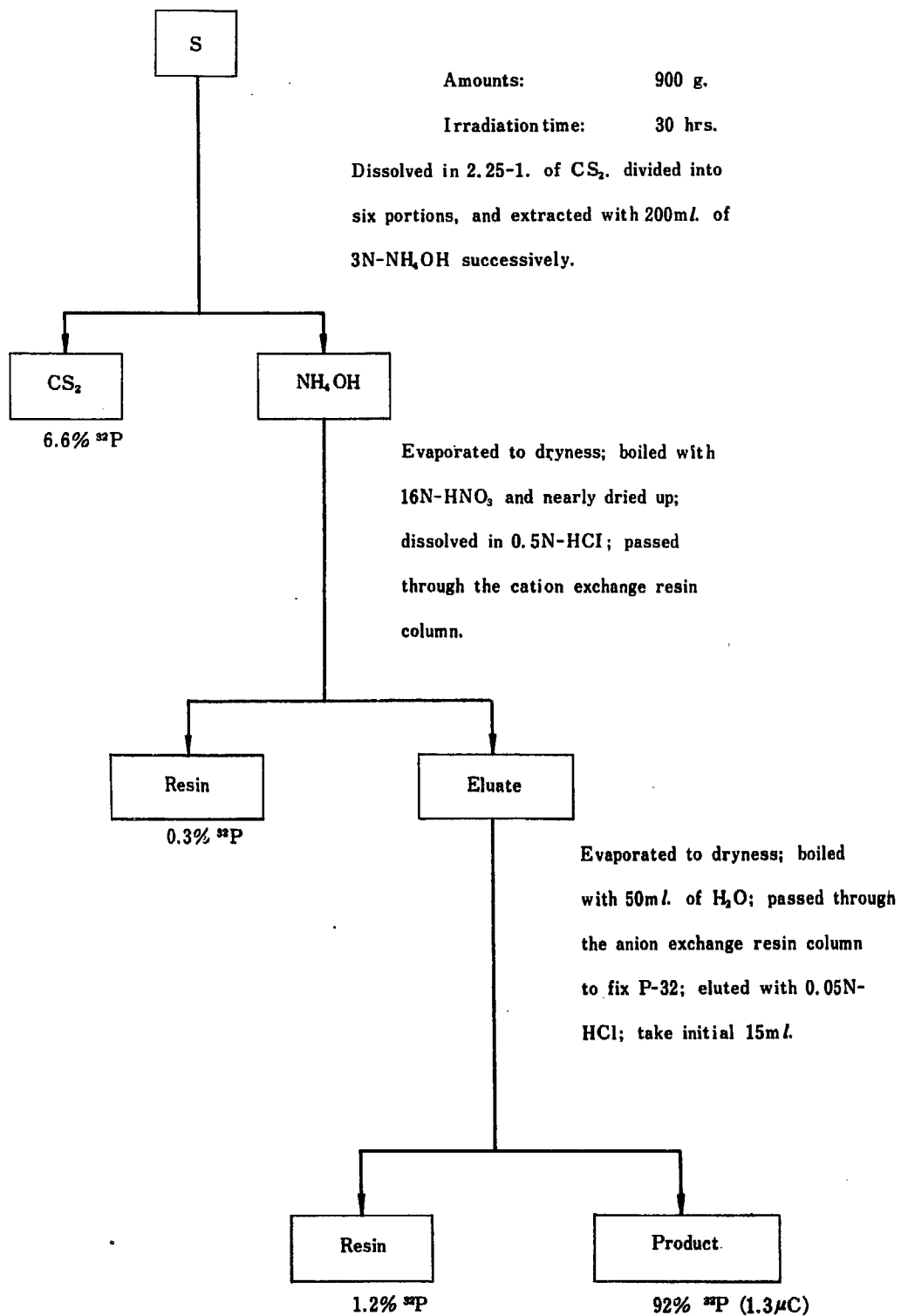


FIG. 5 Flow sheet for the ammonia-ion-exchange process.

3.1 Nitric Acid Process

As shown in Fig. 3, ^{32}P was separated from the large amounts of sulphur by the nitric acid - carbon disulfide extraction and was purified by butyl acetate extraction of phosphomolybdate. The overall recovery of ^{32}P was 75%. The product is a dilute hydrochloric acid solution of $360\mu\text{c } ^{32}\text{P}$. Although ^{32}P is supposed to be in the form of orthophosphate, extraction of molybdenum with TBP makes sure the chemical form of ^{32}P .

During this process, some precautions must be taken for the handling of fuming nitric acid. Fig. 3 shows the flow sheet for this nitric acid process. Further it must be referred that the extraction of ^{32}P with the subsequent purification by ion exchange is another possible way.

3.2 Ammonia - Solvent Extraction Process

Samples were treated according to the flow sheet shown in Fig. 4. This process gave a high recovery of ^{32}P without any special trouble in chemical operations. However, molybdate reagent might bring about an undesired inactive contamination of the product in the routine work.

3.3 Ammonia - Ion - Exchange Process

The flow sheet is given in Fig. 5. In this process, the evaporation of the aqueous solutions is repeated in order to check the cation or anion exchange. Although this repeated evaporation takes a long time, the recovery of ^{32}P is high and reagents which might bring about an inactive contamination of the product are not used in this process.

Based on these reasons, this process is supposed to be the most suitable for routine production of ^{32}P . Accordingly, a glass apparatus shown in Fig. 6 was installed and about 1 kg. of irradiated sulphur was processed with this apparatus. Values for recovery of ^{32}P shown in Fig. 5 were obtained by the process with this apparatus.

As Fig. 5 shows, the glass apparatus consists of three flasks, two ion-exchange columns and other devices. Liquid reagents are added through A_1 , A_2 , A_3 and A_4 . T_1 , T_2 , T_3 and T_4 are glass valves(3) which send solutions from a flask (or column) to another working together with a large syringe.

About 1,000g irradiated sulphur is put into flask I. Sulphur is dissolved in 2.25ℓ of the solvent (added through A_1) by the aid of stirrer S_1 . About 1/10 portion of the resultant organic solution is transferred into flask II through T_1 and shaken with 2N ammonia which is added through A . The mixing is carried out by stirrer S_2 . After settling phases, lower organic layer is

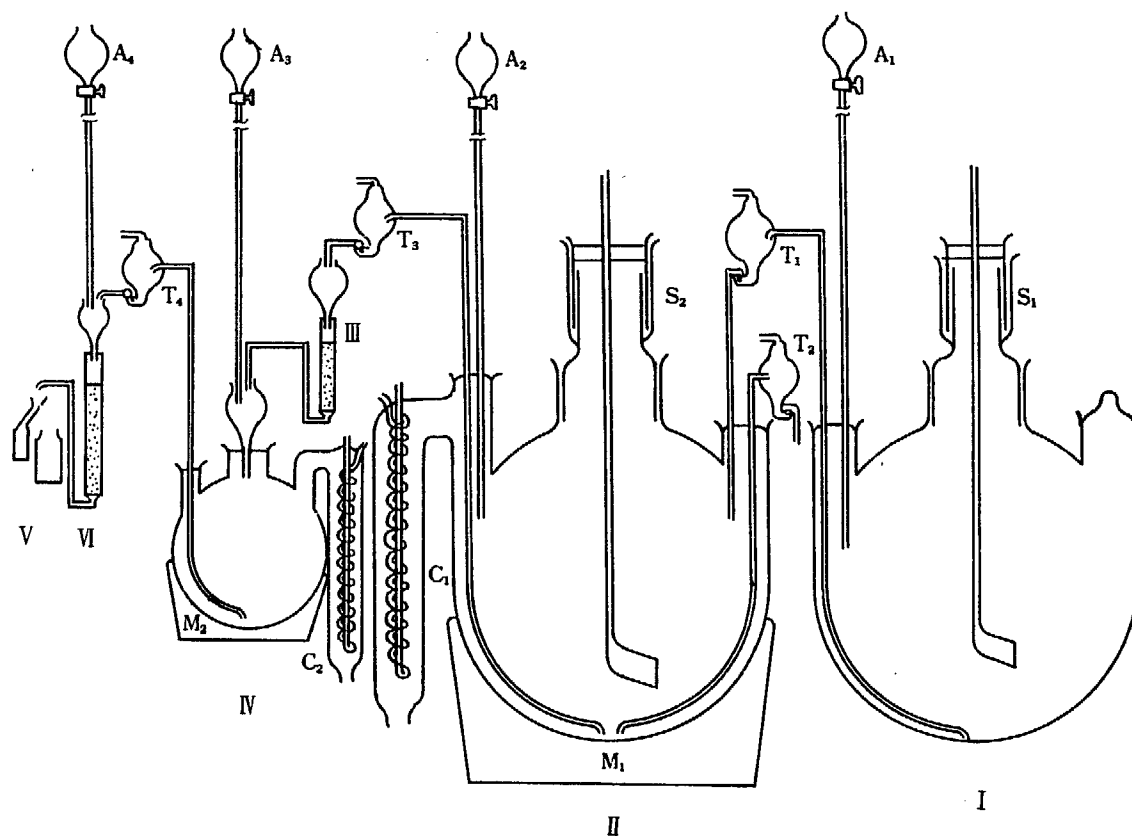


FIG. 6

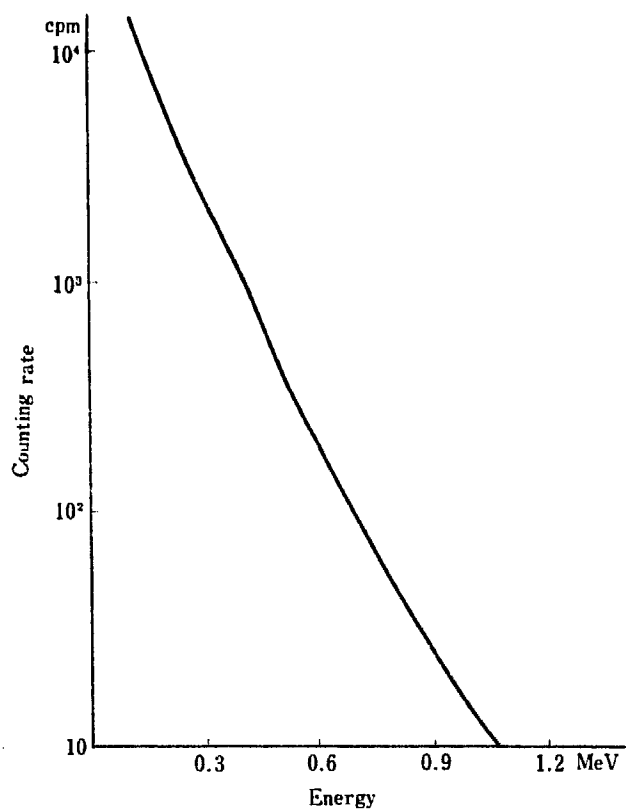


FIG. 7 γ -ray spectrum of the ³²P product.

discarded through T_2 . This scrubbing of ^{32}P with ammonia is repeated against new portions of the organic solution successively until all of them are treated. After the last portion of organic solution is discarded, the remainder of the organic solution is removed by repeated additions of carbon tetrachloride avoiding precipitation of sulphur. The ammonia extract finally obtained in flask II is evaporated by mantle heater M_1 . Ammonia vapor is condensed by condenser C and collected in a receiver. Through A_2 16N nitric acid is added to the evaporation residue in order to make sulfide impurities and colloidal sulphur coagulated. The nitric acid solution is dried up and the residue is dissolved in 0.5N hydrochloric acid again. The resultant hydrochloric acid solution is passed through the cation exchange column III via T_3 . The decationised solution is sent to flask IV and evaporated by heating with M_2 . The residue is dissolved in water which is added through A_3 . The neutral solution resulting is transferred onto anion-exchange column V through T_4 . The solution passed V is discarded. ^{32}P adsorbed on the resin column V is eluted with 15ml 0.05N hydrochloric acid.

4. Chemical and Radiochemical Purities of the Product

The radiochemical purity of the ^{32}P product obtained by any of the three above processes was very high. It was concluded that the product is not contaminated by any γ -emitter because of γ -spectrum of pure bremsstrahlung (Fig. 7). On the other hand, the absorption of β -rays by aluminum (Fig. 8) gives the maximum energy of 1.7MeV which agrees with the generally accepted value for ^{32}P (9). The soft β -rays of long half-life was not found in both absorption and decay curves. The half life of the activity was 14 days according to the decay curve (Fig. 9).

The specific activity is also supposed to be high. Namely, phosphate ion was not found by Feigl's spot test(10). As phosphate is detectable in very low concentration (1 : 20,000) with this spot test, the specific activity of >20 c/g ^{32}P is obtained.

The chemical form of ^{32}P was studied by paper-chromatography. The results certified that 100% ^{32}P is in orthophosphate anion (Fig. 10)

Evaporation residue of the product solution was not noticeable.

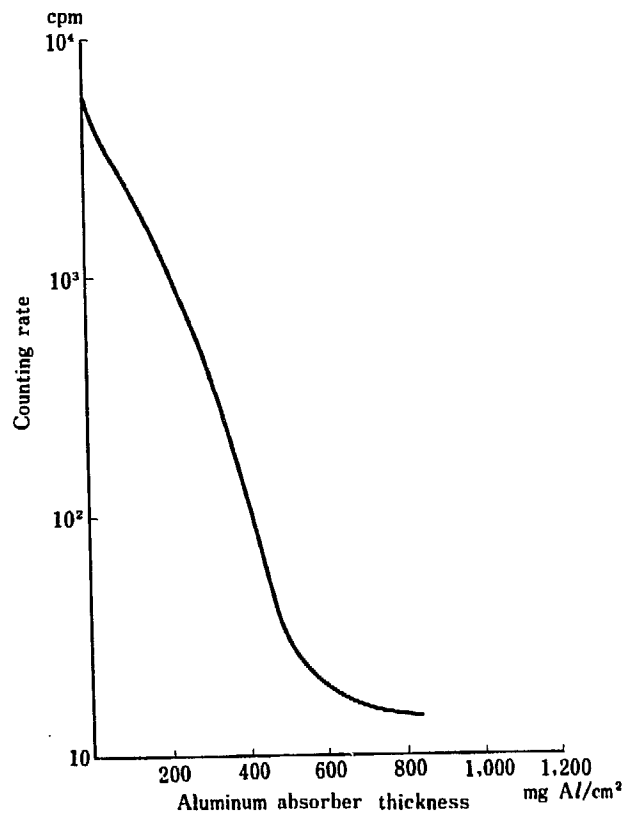


FIG. 8 β -Particles absorption curve of the ^{32}P product.

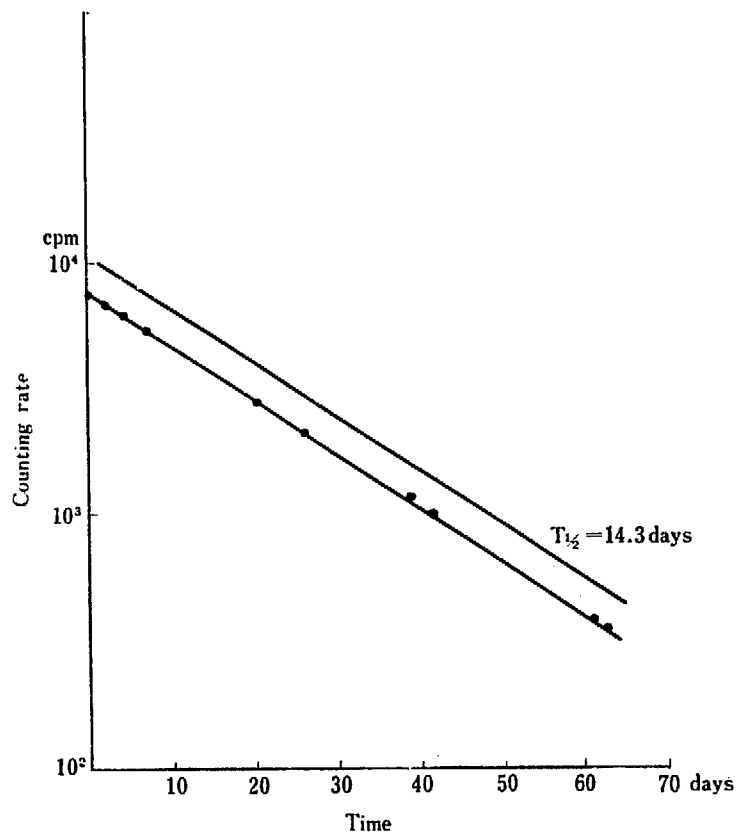


FIG. 9 Decay curve of the ^{32}P product.

5. Estimated Production with JRR-2.

Assuming that the neutron-flux of 10^{13} n/cm²/sec and the continuous irradiation for 240 hrs. are available in JRR-2, a rough estimation gives curie-scale ³²P production for 1 kg. sulphur target in JRR-2.

Supposing the irradiated sulphur is processed according to the flow sheet shown in Fig. 5, the final ³²P solution will show 0.1mg/mc evaporation residue and > 2000c/g^P specific activity because values of evaporation residue and specific activity are only dependent on the way of processing the irradiated target.

Specifications of ³²P products including those estimated values are summarized in Table 3. Qualities of our products seem to be comparable with those of the other countries. But the more detailed data have to be discussed after the operation of JRR-2 or 3.

Though the danger of inflammable carbon disulfide is greatly reduced in this process, we intend to find another process using incombustible bromoform instead of carbon disulfide.

The authors wish to express their indebtedness to Mr. Arai for his valuable assistance.

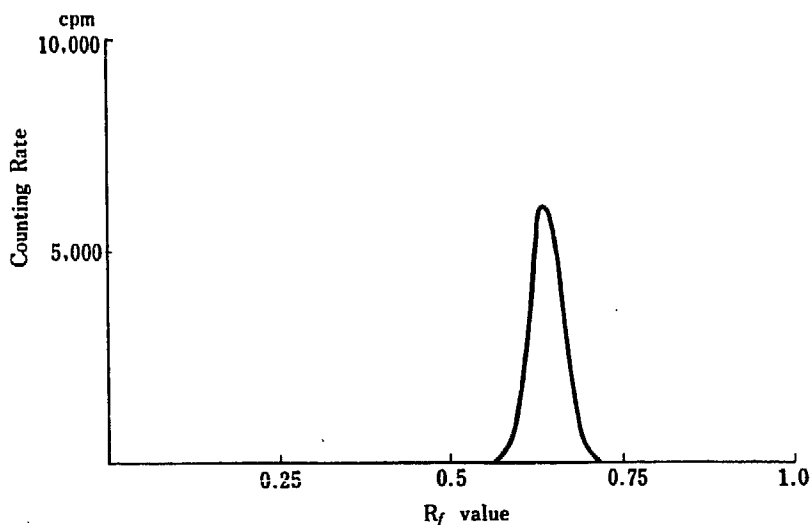


FIG. 10 Paper-chromatogram of the ³²P product.
Developer: n-butanol (2N HNO₃ saturated)

Table 3 Specifications of ³²P products

	Great Britain	Canada	America	Japan
Chemical form	Orthophosphate	Orthophosphate	Orthophosphate	Orthophosphate
Total solid	0.5 mg/ml	1 mg/mc	5 mg/mc	< 0.1 mg/mc ***
Concentration	-----	0.5-25 mc/ml	> 1 mc/ml	20 mc/mg ***
Specific activity	1000 c/g ^P	150-75000 c/g ^P	40 c/g ^P	> 2000 c/g ^P ***
Acidity	PH 2-3	PH 1-3	< 0.5N	----- ***

(Note)

* Observed value when the target was irradiated in JRR-1.

** Calculated value when irradiation will be done in JRR-2.

*** Decided according to the customers' opinions.

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