PRODUCTION OF CARRIER-FREE PHOSPHORUS-32 BY USING SULPHATES AS MATERIAL FOR IRRADIATION

PRODUÇÃO DE FÓSFORO-32, SEM CARREGADOR, USANDO SULFATOS COMO MATERIAL DE IRRADIAÇÃO

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Publicação I E A — N.º **37**

1 9 6 0

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INTRODUCTION

Methods for production of P-32 are usually based on the irradiation of elemental sulphur. The irradiated sulphur requires an acid attack with diluted nitric acid in autoclaves or an attack with fuming nitric acid at atmospheric pres - sure. Specially in the case of fuming nitric acid the reaction is quite vigorous and strong caution must prevail. The aim of the attack with nitric acid is to trans form the formed P-32 into a water soluble species such as phosphoric acid. From this point on the process consists in the separation of elemental sulphur from a phosphate and purification of the later.

A method for the production of P-32 in which the violent attack of sulphur by fuming nitric acid or by dilute nitric acid under pressure could be avoid ed would be desirable. Since the aim of the acid attack is to solubilize the phos- phorus formed, one might start with a material for irradiation that would give the phosphorus in a soluble form from the start of the chemical process. Water soluble sulphates could be used as such starting material. As cation, in the sulphate, a metal with low absorption characteristics for neutrons should be used. Magnesium - seemed to be convenient and magnesium sulphate was chosen as irradiating material .

This same idea of using simpler materials for processing and avoid- ing violent chemical reactions has been adopted by Constant[1] for the processing - of iodine-131. Constant used telluric acid instead of elemental tellurium and avoided, in this way, the difficulties of target dissolution by attacking it with sulphuric and chromic acid mixtures, and later reducing the formed iodate to ele- mental iodine, with oxalic acid.

The disadvantage of using a compound instead of elemental sulphur is that a larger amount of material is required for irradiation; in order to obtain,as far as mass is concerned, the same effect for the irraditation of one gram of sul- phur it is necessary to irradiate about 3.5 grams of magnesium sulphate. However, the simplicity of the chemical process largely compensates for this disadvantage.

Concerning the activity formed after irradiation, the amount of radi oactivity is practically not increased due to the presence of magnesium since the isotopes magnesium-24, magnesium-25 and magnesium-26, in the proportion of 78%, -

10.1% and 11.1% respectively, have the small thermal neutrons cross-sections of 0.03, 0.27 and 0.03 barns, respectively. The main radioisotope formed is magnesi um-27 with a half-life of 9.5 minutes, and a cooling period of 12 hours is suffi - cient for it to decay to a negligible activity.

Chemical process

The magnesium sulphate is irradiated in an aluminum can and the con- tents of the can are removed and transferred to the dissolution flask. For every - 100 grams of magnesium sulphate 150 ml of water is added. The solution is heated to 70°C and 5 ml of hydrogen peroxide 3% is added in order to oxidize the formed P-32 to phosphate. The solution is maintained in agitation for 30 minutes, 0.5 ml of am- monium hydroxide 1:1 is added and then the suspension of magnexium hydroxide is fil- tered through sintered glass of medium porosity and the precipitate is dissolved - with 70 ml of 0.5 M hydrochloric acid. To the solution, ammonium hydroxide is added up to the end point of methyl-orange; the pH is adjusted to 4 with hydrochloric acid and the solution is passed through a cationic ion exchanger in the hydrogen form and the effluent, containing the phosphate ion, is collected.

Apparatus and operations

The apparatus is presented in figure 1. The volumes of the flasks - are for one kilograms of magnesium sulphate. Flask 1 is filled with 1,500 ml of water which is maintained in agitation by bubbling air through tube B. The water in flask 1 is maintained at boiling temperature by the use of an electrical mantle env- olving the flask.

The irradiated magnesium sulphate is added through funnel E. After the sulphate is dissolved, ammonium hydroxide is added through tube C; at the end of C there is a sprayer to wash the flask when the precipitate has been removed. The suspension of magnesium hydroxide and the solution of magnesium sulphate are drawn through the sintered glass filter F, by applying vacuum to flask 2 through G, all other valves being kept closed. Valve G is then closed, valves J and L are opened - and vacuum is applied to flask 3 through valve M. In this way the magnesium sulph - ate solution which has passed through filter F is transferred to flask 3.

After the magnesium sulphate is transferred to flask 3, valves J and L are closed, valves O and D are opened and pressure is applied to flask 3 through M ; the magnesium sulphate solution is then transferred to flask 1 for a new precipita - tion, if necessary.

The magnesium hydroxide precipitate collected at F is washed with water through tube and valve H; water from the washing is removed through J and L the same way the solution of magnesium sulphate was transferred from flask 2 to flask 3. Next the magnesium precipitate in F is dissolved with hydrochloric acid through valve and Tube H.

The magnesium chloride solution, in which the phosphorus-32 is present- as a soluble phosphate, is transferred to flask 4 by opening valves J and K and apply ing vacuum to flask 4 through valve Q.

The magnesium chloride-labelled phosphate solution is passed through a cationic ion-exchanger, in hydrogen form, by opening valve S and collected in beaker- T which is maintained on a water bath. In such a way the solution is being concen - trated to a small volume at the same time it is being collected from the resin. The evaporation of the solution is continued until dryness and the phosphoric acid, which is carrier free, is dissolved with a solution of hydrochloric acid of desired concen tration. If carrier of phosphorus is not inconvenient, the required amount of sodium phosphate is added at this point.

The stock solution of 0.5 M hydrochloric acid, 1:1 ammonium hydroxide - and water for washing, are kept outside the lucite-shielded hood in kitasato flasks provided with rubber pressure bulbs that allow the transfer of the liquids to the re- quired flask.

The regeneration and washing of the cationic resin is made through tu- be R.

All stoppers indicated in the drawing are of ground-glass type. The various valves are the burette types.

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Yields

An evaluation of the chemical yield for the proposed process can   be made, with a good approximation, by measuring the activity in the magnesium sulphate before processing and comparing it with the activity of the isolated P-32 after   the chemical process. In order to calculate the yield, 10 grams of magnesium sulphate   were irradiated for 3 hours in a flux of fast neutrons corresponding to 0.35×10^{13} neutrons/sec.cm^2. After a cooling period of eight days an aliquot of 0.1264 grams of irradiated magnesium sulphate was dissolved in water and the volume made up to 25 ml; aliquots of this solution were evaporated under an infra-red lamp in copper planchets and mounted for counting. The activity observed can be ascribed only to P-32 since the short irradiation time and the cooling period of eight days would make the   contribution due to isotopes of magnesium and sulphur negligible. The isotopes of mag- nesium that might interfere with the counting would be magnesium-27 with a half-life of 9.5 minutes but this activity is reduced to a very low value after the cooling pe- riod. Sulphur-35, with a half-life of 87 days, might also give a contribution; how - ever, the short irradiation period would not allow the formation of large amounts of this isotope since the isotopic percentage for sulphur-34 is only 4.2% and its cross- section for the (n, gamma) reaction is 0.26 barns. In any case, the sample of irra - diated magnesium sulphate and of separated P-32 were both counted with an   aluminum- absorber of 80 mg/cm^2. The ratio of the values obtained for the P-32 activity after- processing to the activity in the unprocessed magnesium sulphate gave a yield of 83%. The determination of the yield for other operations gave an average value of 85%.

In order to check the amount of activity corresponding to P-32   that was not recovered on the first set of operations, the liquid in 3, obtained as   the filtrate of the first precipitate of magnesium hydroxide, was returned to flask 1 for a new precipitation. The process was repeated four times and the results are present- ed in Table I.

TABLE 1

Number of precipit- ation of Mg(OH)$_2$	Percentage of P-32 separated
1st	83.0
2nd	10.5
3rd	4.7
4th	0.8

Contaminants

The chief contaminants found in the process of elemental sulphur treatment by nitric acid processes, are the main constituents of stainless steel, meaning, iron, chromium, and nickel. Corrosion of the stainless steel extraction equipment occurs from sulphuric acid which is formed by the action of the nitric acid on sulphur. Chromium, most of which is absorbed in the cationic resins, holds up large quantities of activity, in accordance with Butler and Gissel[2]. The attack with nitric acid usually gives small amounts of silica after the final evaporation of the product solution and a fine sintered glass filter must be used in order to remove this precipitate.

None of these contaminants were found in the present proposed method. Stainless steel is not used in the apparatus and silica does not appear in the final products, since the dissolution of the irradiated magnesium sulphate is made in a very suave operation.

Sulphate ion may be found as a contaminant in the final labelled phosphoric acid solution, since some sulphate is entrained with the magnesium hydroxide - precipitate. However, sulphate can be reduced to a very small amount by evaporating the phosphoric acid solution on a hot plate until no more white fumes of SO_3 are detected.

Discussion

Although, as said before, there is the inconvenience of using a larger mass for irradiation, this is not a draw-back for the process. The apparatus used is very simple, inexpensive, the reaction is not a violent one, there is no attack of metallic parts of the hood and of the equipment by fumes of nitric acid, it is not necessary to use auto-claves (stainless steel), there is no danger of contaminating the pipe lines of the exhaustion system with particles of sulphur that might be entrained with the vapors of nitric acid (when using the process of fuming nitric acid), and - the yield of the process is quite high.

Some experiments had been run by using lanthanum, as carrier for the phosphate, on the operation of the magnesium hydroxide precipitation. Lanthanum is

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usually used as carrier on the process in which elemental sulphur is the irradiating
material, and the final separation from the phosphate is made on the cationic   ion
exchanger by retaining the lanthanum in the exchanger. The use of lanthanum as car-
rier, in the present process, and precipitation of magnesium and lanthanum hydroxide
did not improve the process. In fact some lanthanum would always pass through   the
cationic resin without being absorbed and would appear as impurities on the   final
phosphate solution. This did not happen with magnesium; by adjusting the pH of the
solution to a value corresponding to the end point of methyl-orange a quantitative ·
absorption of magnesium ion would be obtained and the final solution of phosphate ·
would not be impurified by magnesium.

Determination of the half-life of the separated **P-32**, as well as ener-
gy of its beta particles and gamma spectrometry scanning showed that, by using ana-
lytical grade magnesium sulphate no radiochemical impurities would appear in the   ·
phosphate. The contaminants usually found in the process in which elemental sulphur
is attacked by nitric acid, meaning, iron, chromium, nickel and silica are not found
in the process. Magnesium was quantitatively absorbed on the cationic exchanger and
did not contaminate the phosphate solution.

SUMMARY

This paper presents a method for producing P-32 by using material for
irradiation other than elemental sulphur. The set of chemical operations, apparatus
yields, and advantages are described.

REFERENCES

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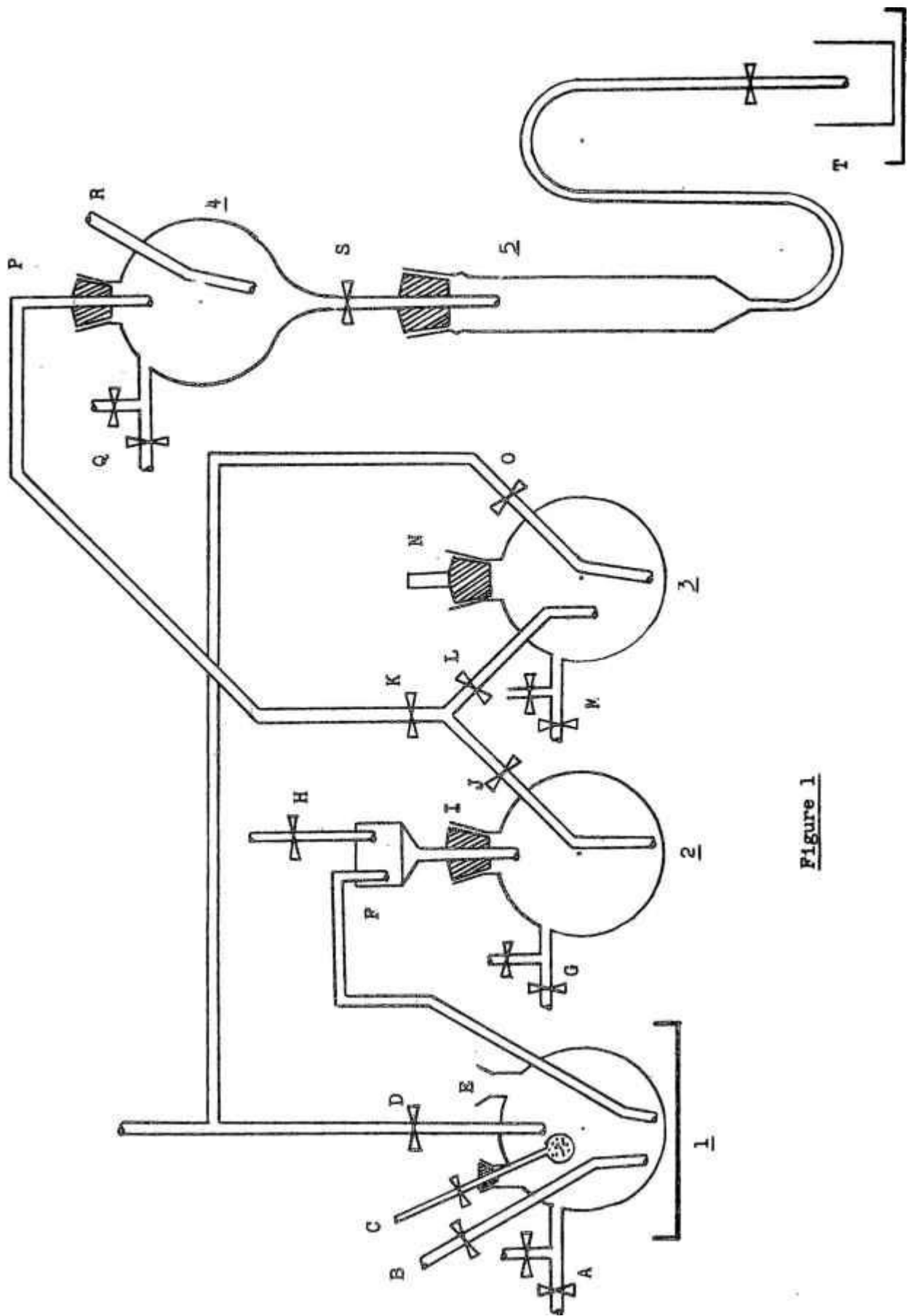2) Butler and Gissel - Separation of P-32 from sulphur-32 - AECD-2850.

Figure 1