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PREPARATION OF CARRIER-FREE LANTHANUM-140

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ABSTRACT

Tracer methods for La find limited usage because of the short half life (40-hr) of the radioisotope La^{140} . A continual supply of carrier-free La^{140} can be obtained by "milking" it at intervals of a few days from its parent, Ba^{140} (12.8-day half life). Ba^{140} is precipitated with barium nitrate carrier from 80% nitric acid, and La^{140} is recovered from the filtrate. A yield of about 90% was obtained, and high purity was indicated by the fact that the La^{140} decayed with a 40-hr half life for about 15 days. By use of this method, a tracer supply of La^{140} is available for several weeks from an initial source of a few millicuries of Ba^{140} . A modified filter-beaker, specially adapted for radiochemical work, is described.

INTRODUCTION

The determination of lanthanum in rare earth mixtures is complicated by the difficulty of distinguishing its properties from those of other cerium earths. In fact, lanthanum is usually determined by difference after the mixture has been analyzed for other rare earth elements.^{1, 2} Analytical methods based on oxidimetry, such as is used for cerium,³ praseodymium,⁴ and europium,⁵ cannot be applied, since an oxidation state other than three is unknown for lanthanum.^{6, 7} Lanthanum salts have no characteristic absorption bands in the visible spectrum; therefore, spectrophotometric methods such as Moeller and Brantley⁸ and Rodden^{2, 9} used for many of the rare earths are not possible.

Radioactive tracer methods¹⁰ can be used for the determination of lanthanum. Lanthanum-140, a beta-emitter which decays to stable cerium-140, seems to be the most practical isotope for tracer experiments; but, because of its relatively short half life of 40 hours,^{11, 12, 13} its use is limited in most laboratories. However, a continual supply of carrier-free lanthanum-140 can be obtained by "milking" it at intervals of a few days from its parent isobar, barium-140,^{14, 15} which has a considerably longer half life, 12.8 days,¹⁶ than lanthanum-140. Schweitzer and Jackson¹⁷ separated carrier-free lanthanum-140 from barium-140 by the formation of a radiocolloid of lanthanum in basic solution. The radiocolloid was filtered on a fine fritted-glass filter. However, some barium-140 was carried by the colloidal lanthanum-140, and the method had to be repeated several times to obtain the desired purity. High yields were obtained only if special precautions were taken against the introduction of carbonate and the absorption of carbon dioxide. Carrier-free lanthanum-140 also has been separated by precipitation on ferric hydroxide, with barium holdback carrier used to retain the barium-140 in solution.¹⁵ This method requires at least a double precipitation of the ferric hydroxide, and the slightly high half life value which was reported for the lanthanum-140 (40.9 hours) indicates that a radioactive impurity was still present. Ion-exchange has been used to prepare carrier-free lanthanum-140;^{18, 19} however, the method is too time-consuming to be practical.

In this paper, a method is given for obtaining carrier-free lanthanum-140 which is based on the low solubility of barium nitrate in 80 per cent nitric acid^{20, 21} as compared to the relatively high solubility of lanthanum nitrate.²² Barium-140 is precipitated with barium nitrate carrier from 80 per cent nitric acid, and carrier-free lanthanum-140 is recovered from the filtrate. The barium nitrate precipitate is set aside for a few days to allow lanthanum-140 to grow in. When additional lanthanum-140 is needed, the barium nitrate is dissolved and reprecipitated from 80 per cent nitric acid. In this way, a tracer supply of lanthanum-140 is available for several weeks from an initial source of a few millicuries of barium-140.

REAGENTS

Barium-Lanthanum-140

Ten millicuries of barium-lanthanum-140 equilibrium mixture as the chlorides in 10 milliliters of dilute hydrochloric acid solution was obtained from the Radioisotopes Division of the Oak Ridge National Laboratory. The isotopes were reported to be carrier-free. The only radioactive impurity reported was strontium-89, which was present in the amount of 1.44×10^{-4} millicurie per milliliter.

Nitric Acid

The concentrated (70%) nitric acid was analytical reagent grade. The red fuming nitric acid was Baker and Adamson reagent grade and assayed 93.1% HNO_3 and 7.05% N_2O_5 .

Barium Nitrate

Reagent grade barium chloride was dissolved in water, and barium nitrate was precipitated by adding concentrated nitric acid. Impurities which were soluble in concentrated nitric acid were thus removed. The barium nitrate was filtered in a sintered-glass funnel, washed with a small quantity of water, and dried at 110°C .

RECOMMENDED PROCEDURE

Add two milliliters of water to 0.5 gram of barium nitrate. Spike the mixture with barium-lanthanum-140. Heat and stir until all the barium nitrate has dissolved. (If necessary, add a few additional drops of water.) Reprecipitate the barium nitrate by the dropwise addition of two milliliters of concentrated nitric acid. Evaporate with stirring until the volume of the mixture is approximately two milliliters. Cool in an ice bath and add three milliliters of red fuming nitric acid. Digest in an ice bath for 15 minutes with stirring. Filter the barium nitrate and discard the filtrate. Set the barium nitrate aside for several days.

After fresh lanthanum-140 has grown in, dissolve the barium nitrate in two milliliters of water. Reprecipitate the barium nitrate from 80 per cent nitric acid as described above. Filter the barium nitrate, but do not wash it. Evaporate the filtrate to dryness in a small beaker (20 or 30 ml). Dissolve the slight residue in dilute nitric acid and dilute to the desired volume. Save the barium nitrate for future "milkings".

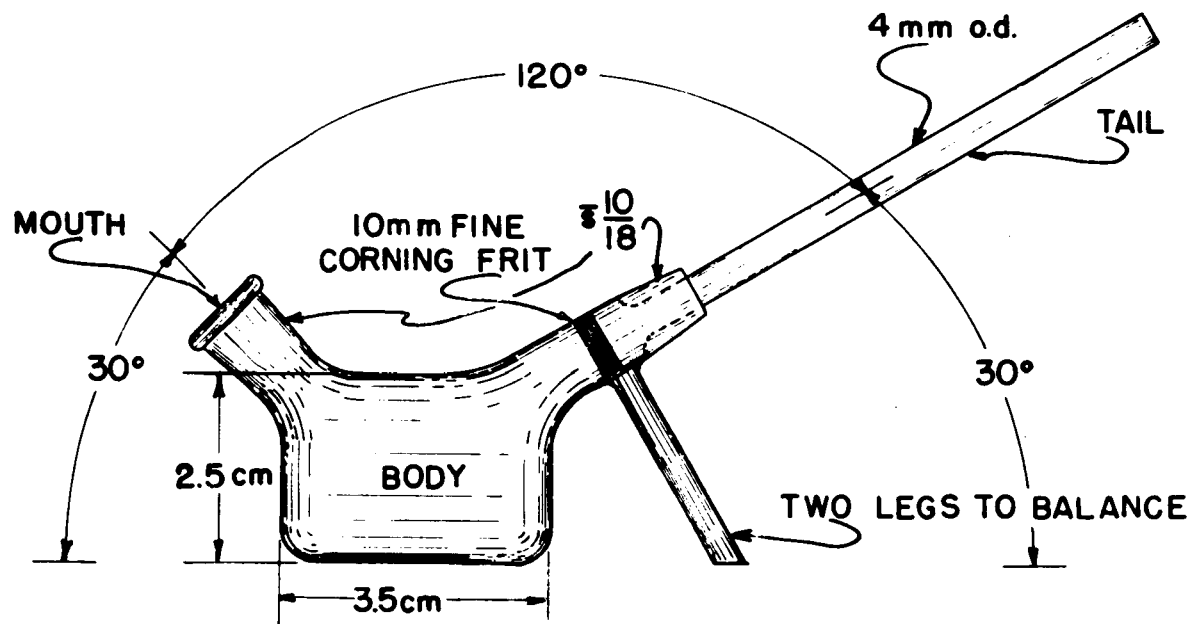
One millicurie or less is a convenient quantity of barium-lanthanum-140 to use. Larger quantities can be used with personnel shielding. The first "milking" of lanthanum-140 was discarded, since this fraction contained any impurities in the original barium-140 which were soluble in 80 per cent nitric acid. The lanthanum-140 which then grew in was free of these impurities. It is recommended that at least four or five days be allowed between successive "milkings". It is suggested also that fresh barium nitrate be used with each new shipment of barium-140.

APPARATUS

The recommended procedure can be carried out in small beakers, with small sintered-glass funnels used for the filtrations. However, the separation is more conveniently made in a modified filter-beaker (Fig. 1), which will hereafter be referred to as an "animal".

6

fig 1



MODIFIED FILTER-BEAKER (ANIMAL)

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The operation of an animal during a precipitation is shown in Figure 2. Reagents are added through the mouth of the animal with a medicine dropper. Stirring is effected with a magnetic stirrer. A piece of iron nail sealed in glass makes a convenient stirring bar. Heat is supplied by an infrared lamp. Evaporation is somewhat slow but can be speeded up by placing the animal on an asbestos pad, by painting the bottom of the animal black with a suspension of colloidal graphite in water, or by passing a stream of dry, warm air through the tail of the animal. For filtrations, the animal is rotated 120° and inserted into a small bell jar fitted with a standard taper joint (Fig. 3) or, if needed, into another animal.

The barium nitrate, which is never removed from the animal, may be redissolved by back-washing the frit with water. This is accomplished by applying suction to the mouth of the animal and adding water through the tail by means of a transfer pipette (a medicine dropper with the dropping end drawn down to a capillary tube).

The animals are excellent radiochemical equipment because they keep the radioactive material confined, thereby reducing contamination. They are equipped with interchangeable standard taper joints so that they may be used in series.

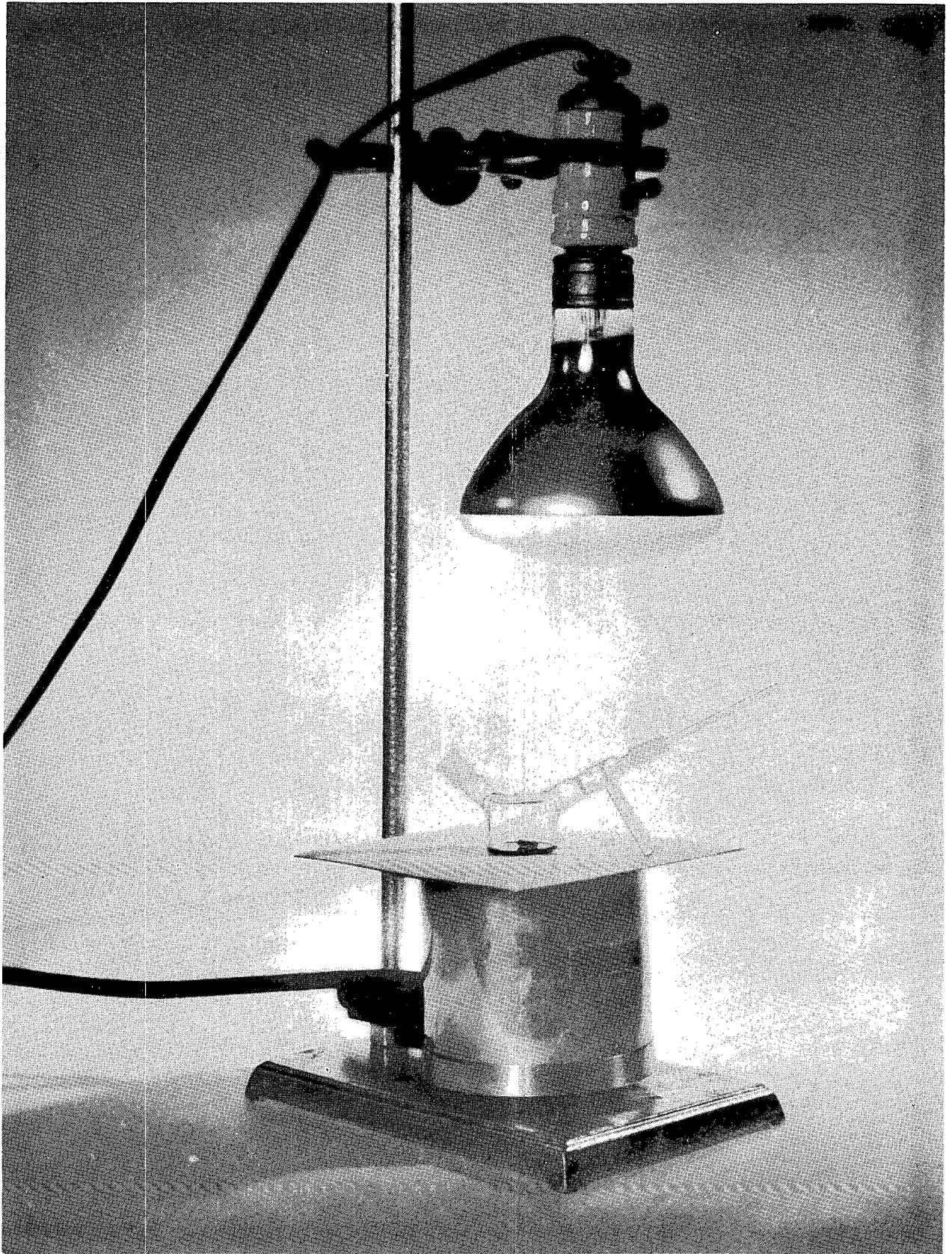
DISCUSSION

The purity of the carrier-free lanthanum-140 prepared by the recommended procedure is indicated by its decay curve (Fig. 4). Samples of the lanthanum-140 were mounted on two-inch stainless steel disks, and the beta activity was counted periodically in a Nuclear Measurements Corporation Model PC-1 Proportional Counter. No appreciable deviation from the decay curve was observed for a period of about 15 days. After this length of time, only 0.2 per cent of the original lanthanum-140 remained. The half life value of 40.5 hours, determined by the method of least squares,^{11, 12, 13} is within one per cent of the accepted half life value of 40.0 (± 0.1 to 0.5) hours.

An average yield of 75 per cent was obtained when the separation was carried out in beakers, whereas in an animal the yield was 88 per cent. Higher yields can be obtained if the barium nitrate precipitates are washed with 80 per cent nitric acid, but this also increases slightly the amount of barium-140 impurity. As high purity is thought to be the more important factor, the recommendation is made that the precipitates not be washed. The remainder of the lanthanum-140 is not lost but stays with the barium-140.

The quantitiveness of precipitation of barium nitrate in 80 per cent nitric acid was determined by analyzing the filtrates for barium-140 by the method of differential decay.²³ The average barium concentration in the 80 per cent nitric acid filtrates was 0.013 milligram of barium per milliliter. Since the total volume was five milliliters and about 250 milligrams of barium carrier was used, the amount of barium-140 remaining in the filtrate as a radioactive impurity in the lanthanum-140 was found to be approximately 0.03 per cent.

The recommended procedure is particularly effective for preparing carrier-free lanthanum-140, because only strontium, barium, radium, and lead form insoluble nitrates in 80 per cent nitric acid.²¹ Hence, the lanthanum-140 which grows in after the first "milking" need be separated only from these elements and their daughter activities. Radium and lead were both found to be absent, since the alpha activity in the lanthanum-140 mounts did not differ significantly from background. (All radioactive isotopes of lead and radium have alpha emitters in their decay chains.) The quantity of barium has been shown to be very low, and the same is probably true for strontium.²¹



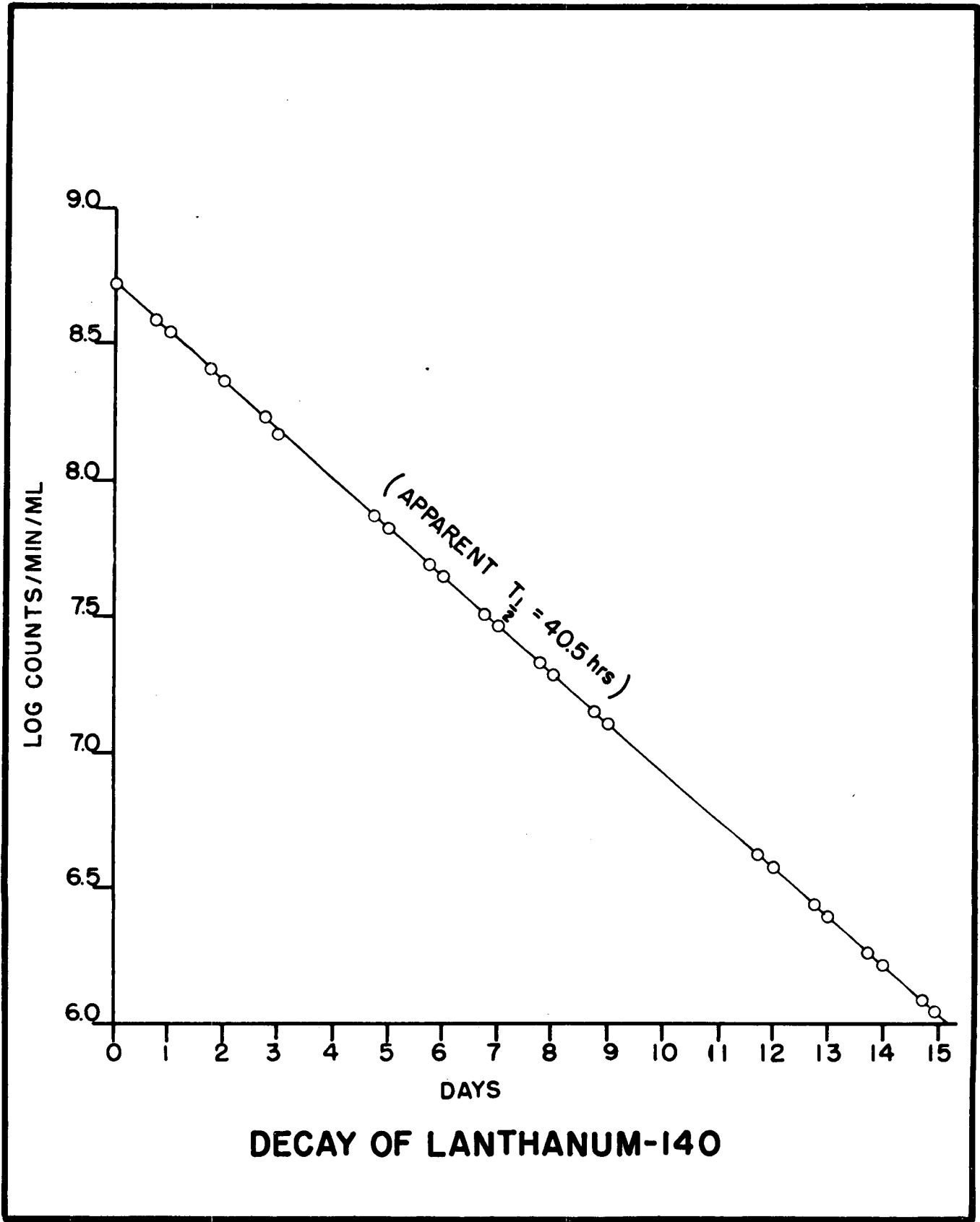
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SET UP FOR REACTION IN AN ANIMAL



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FILTRATION IN AN ANIMAL



A more highly purified lanthanum-140 has been prepared by using a double barium chromate precipitation from homogeneous solution to separate any strontium, followed, after the lanthanum-140 has grown in, by a double nitrate precipitation to remove the barium. In the chromate precipitations, strontium holdback carrier is used and precipitation of barium chromate is effected homogeneously by neutralizing nitric acid solutions of the chromates with potassium cyanate.²⁴ The second nitrate precipitation is made by adding 0.5 gram of barium nitrate to the lanthanum-140 prepared by the recommended procedure and repeating the procedure. This highly purified lanthanum-140 was used to determine a precise half life value, and the results of this experiment will be reported elsewhere.²⁵

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