ON THE PREPARATION OF THE NEUTRON-DEFICIENT Nb\(^{92}\) IN HIGH SPECIFIC ACTIVITY

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Received October 15, 1962

(Communicated by Dr. B. V. Thosar, F.A.S.C.)

INTRODUCTION

The neutron-deficient isotope Nb\(^{92}\) (10.1 d) was required in high specific activity for nuclear spectroscopic studies in this Laboratory. The following aspects of this problem had to be tackled: (i) to produce sufficient amount of the isotope by a nuclear reaction in a neighbouring element, (ii) to separate the Nb\(^{92}\) activity in the carrier-free and pure form from the target material, and (iii) to check the radiochemical purity of the sample. We have made an attempt to produce sufficient amount of Nb\(^{92}\) by \((n, p)\) reaction in Mo\(^{92}\) using natural molybdenum as the target. Irradiation was done in the fission neutron flux in the reactor "Apsara" at Trombay. Previous measurements\(^1-3\) in the reactors at Harwell and Chalk River indicate that the reaction Mo\(^{92}\) \((n, p)\) Nb\(^{92}\) has got an appreciable cross-section in a fission neutron flux. Our measurement\(^3\) of this cross-section in the spectrum of neutrons at "Apsara" gave the value of 7.5 mb.

The major activity produced in the irradiation of molybdenum is Mo\(^{99}\) (66 h) produced by neutron capture in Mo\(^{98}\). Since this cross-section is several orders of magnitude higher than the \((n, p)\) cross-section, the problem of chemical and radiochemical purity involves specific separation from molybdenum.

The method used for the separation of carrier-free Nb\(^{95}\) from fission products involves extraction of the cupferron complex of niobium by chloroform.\(^4\) But in this step molybdenum is also extracted quantitatively.\(^5-6\) Whereas in the case of fission product Nb\(^{95}\) (35 d) the separation can be done after Mo\(^{99}\) activity has died out completely, it cannot be done in the case of Nb\(^{92}\) produced by neutron irradiation of molybdenum. The Nb\(^{92}\) thus produced will also contain some amount of Nb\(^{95}\) (23 h) and Nb\(^{95}\) (35 d) produced

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by \((n, p)\) reaction in Mo\(^{94}\) and Mo\(^{95}\) respectively present in the natural molybdenum in comparable abundance to that of Mo\(^{92}\). Since these cross-sections as measured by us\(^4\) are much smaller than that for Mo\(^{92}\) \((n, p)\) Nb\(^{92}\), the contamination of Nb\(^{92}\) by these activities is not appreciable if the length of irradiation and the time of cooling of the target after irradiation are chosen judiciously. The radiochemical purity of the prepared sample could be checked by a study of its gamma-ray spectrum.

**Experimental**

**Extraction of niobium by di-isobutyl ketone.—**Niobium has been found to get extracted as the chloride complex into di-isopropyl ketone\(^7\) in macro and semi-micro quantities. This method has been utilised for quick radiochemical separation of short-lived niobium activities in fission.\(^8\) Here we have investigated the extraction of the chloride complex of niobium into di-isobutyl ketone (DIBK). For the preliminary studies a tracer of Nb\(^{95}\) produced by milking from fission-produced Zr\(^{95}\) sample with 5 mg. niobium carrier, was used. Later these measurements were repeated using carrier-free tracer of Nb\(^{92}\) produced by the method given here. The distribution ratios of radio-niobium between DIBK and hydrochloric acid of different molarities were found out by equilibration and finding out the concentrations of radio-niobium in the aqueous and organic phases. The radio-niobium from each phase was separated with 5 mg. niobium carrier and counted as Nb\(_2\)O\(_5\) in a methane-flow proportional counter. The percentage of niobium extracted into DIBK was calculated at different molarities of hydrochloric acid at room temperature and also for hydrochloric acid saturated at 0°C with dry hydrogen chloride gas (ca. 13 M). The results are shown in Fig. 1. It can be observed from the figure that niobium is extracted at high concentrations of hydrochloric acid, while it can be back-extracted by 6 N hydrochloric acid. This method is incorporated in the chemical procedure for the separation of Nb\(^{92}\).

**Dissolution of target.—**Irradiated molybdic acid is found difficult to be dissolved either in hydrochloric acid or in conc. ammonia. A blue mixture is produced in either case. This is due to the radiation damage produced by the intense irradiation. The material can be made to dissolve by heating with conc. nitric acid till the whole mass is turned completely white. The product is then easily dissolvable in conc. ammonia.

**Decontaminations.—**Neutron-irradiated molybdenum is found to contain appreciable amount of Co\(^{60}\), produced by \((n, \gamma)\) reaction in traces of cobalt impurity. This cobalt activity is partly co-séparated along with the niobium.
ard is a contaminant in the Nb$^{92}$ thus produced.$^9$ This can be avoided by adding cobalt hold-back carrier during the co-precipitation of niobium by ammonia. Similarly La$^{140}$ is also found to be a contaminant in the Nb$^{92}$. This can be separated by La F$_3$ scavenging step.$^{10-11}$ By separating the cobalt and lanthanum activities separately and measuring their activities in a scintillation counter it is found that 5 p.p.m. of cobalt and 3 p.p.m. of lanthanum are present as impurities in the molybdic acid.

Decontamination from Zr and possible rare-earth activities is effected by La F$_3$ and Ba Zr F$_6$ precipitations in the usual way.$^{10-11}$ Technitium can be removed by a copper sulphide scavenging from 3–4 $M$ sulphuric acid solution,$^{12-13}$ in which technitium is co-precipitated.
Details of Procedure

Target: 2 gm. molybdic acid irradiated in the reactor for 5 days and cooled for 2 days.

1. Heat the target material with 2–3 ml of fuming HNO₃ in a 40 ml. conical centrifuge tube till the colour turns completely white. Cool.

2. Add 10–15 ml of conc. ammonia solution and stir well till completely dissolved.

3. Add 10 mg. each of Fe, Zr and Co carriers. Stir well and let stand for 2 minutes. Centrifuge and discard the supernate.

4. Wash the precipitate with distilled water containing ammonia and ammonium chloride. Centrifuge and discard the washings.

5. Dissolve the precipitate in 2 ml. of fuming HCl. Dilute to 10 ml. Add 10 mg. Mo hold-back carrier, and conc. ammonia to precipitate the hydrous oxides. Centrifuge and discard the supernate. Wash the precipitate with water containing ammonia and ammonium chloride. Discard the washings.

6. Repeat step 5 six times. The precipitate should not be coloured with adsorbed Co⁺⁺ ion.

7. Dissolve the precipitate in 2 ml. of conc. HCl, dilute to 10 ml. Make 5 N in HF and 5 N in HNO₃. Precipitate BaZrFe₆ by adding BaCl₂ solution containing 50 mg. Ba/ml. Centrifuge and discard the precipitate. Repeat the BaZrFe₆ precipitation once more by adding 10 mg. Zr carrier and BaCl₂ solution. Centrifuge and transfer the supernate to a 125 ml. separatory funnel.

8. Destroy the HF by adding 15 ml. of saturated boric acid, make 1 N in HCl. Cool in ice. Add 2 ml. of 6% cupferron reagent, shake and extract with 10 ml. of chloroform. Collect the chloroform layer in a 125 ml. conical flask. Add 2 ml. of cupferron reagent to the aqueous phase and extract with 10 ml. of chloroform. Collect the chloroform layer in the same conical flask.

9. To the organic phase add 2 ml. of conc. H₂SO₄ and 20 ml. of fuming HNO₃. Boil till the organic matter is completely destroyed. Transfer the solution to a conical centrifuge tube, centrifuge if the solution is not clear.

10. Make the solution 3-4 N in H₂SO₄. Add 10 mg. of Cu carrier and pass H₂S till saturation. Filter through a Whatman No. 1 filter-paper,
collecting the filtrate in another 40 ml. centrifuge tube. From the supernate reprecipitate the hydrous oxides by adding ammonia. Centrifuge and wash the precipitate with distilled water.

11. Dissolve the precipitate in 5 ml. of fuming HCl. Cool in ice, saturate with dry hydrogen chloride gas at 0° C. Transfer to a 25 ml. separatory funnel. Extract twice with equal volumes of DIBK, previously equilibrated with fuming HCl saturated with hydrogen chloride gas at 0° C. From the organic layer back-extract niobium by 10 ml. of 6 N HCl. Evaporate

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**Fig. 2.** Gamma-ray spectrum of the separated Nb⁵⁺.
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the HCl phase containing carrier-free niobium. The iron will be retained in the organic phase.

Time for the separation: 4-5 hours.

Comments.—The procedure gives excellent decontamination from all the possible impurities. The gamma-ray spectrum of the sample (Fig. 2), taken in a 3" dia. × 3" thick NaI(Tl) crystal and DuMont 6363 photomultiplier and a Nuclear Data 512 channel pulse height analyzer, shows the 930 and 1830 keV gamma-rays$^{14}$ of Nb$^{92}$ only. From the possible contribution of the 740 keV photopeak of Mo$^{99}$ in the spectrum of the separated Nb$^{92}$ and the unseparated molybdenum target, the decontamination factor from molybdenum is found to be at least 10$^8$. Decontamination from Zr, Co, La and Tc is also excellent. The chemical yield was determined in a typical run by separating Nb$^{92}$ from equal amounts of the target from the same irradiation, with and without carrier and measuring the activities. It is found to be more than 90 per cent. In a representative separation 5.5 μc. of Nb$^{92}$ was obtained per gram of molybdenic acid irradiated for 5 days and cooled for 3 days. The amount of foreign matter present in the sample was less than 0.2 mg.

SUMMARY

The extraction of niobium by di-isobutyl ketone from hydrochloric acid solutions is investigated. This method is made use of in the preparation of the neutron-deficient Nb$^{92}$ in high specific activity. Nb$^{92}$ is produced by (n, p) reaction in Mo$^{99}$ using natural molybdenum irradiated in the reactor. The effect of (n, p) reactions in other naturally present isotopes of molybdenum, on the radiochemical purity of the sample, is discussed.

ACKNOWLEDGEMENTS

The author is thankful to Professor B. V. Thosar for his interest in the work. He is also grateful to Dr. H. D. Sharma and Dr. M. V. Ramaniah for permission to use the proportional counter and to Mr. M. N. Namboodiri and Mr. N. Ravindran Nair for their help in some of the measurements. The assistance of Miss M. Radha in the later stage of the work is gratefully acknowledged.

REFERENCES


