Abstract:

Neptunium

Nowadays it is well known that element 93, Neptunium, shows chemically similar behavior to element 92, Uranium. Furthermore, it is known that both of these elements are part of a special group, the actinides, similar to the lanthanides or ‘rare earth elements’. These groups are different from the transition metals in regards to their chemical behavior. This was first shown by McMillan and Abelson (Phys.Rev.57, 1985(1940)). Their experiments showed the similarities in behavior of Neptunium compared with Uranium and Thorium. Under basic conditions Neptunium precipitates in the tetravalent state as Neptunium hydroxide regardless of the presence of carbonate anions. In the hexavalent state it forms soluble carbonate complexes. Both of these behaviors are found in Uranium as well. Thorium and Neptunium can be precipitated as iodates in the tetravalent state. McMillan and Abelson also checked for the similarities between Neptunium and Rhenium, because the former should have been a heavier homologue of the latter if the actinides didn’t exist and these elements would therefore instead be transition metals. The experiment showed that there is no significant similarity between Rhenium and Neptunium. It is for example possible to precipitate Rhenium ions with sulfide, while Neptunium stays soluble. With these experiments and more it was possible to determine that there indeed seems to be a special group in the periodic table which Neptunium, Uranium and Thorium are part of.

In this lab course some of these historically significant experiments are to be conducted by the participants.

The goal of this course is to give the participants a sense of the practical aspects of nuclear chemistry, in regards to the safety issues, problems that might occur while doing chemical reactions as well as a basic understanding of the chemical behavior of actinides form an experimentalist perspective.

Transuranics - The Chemistry of Neptunium

- Literature:Keller, pp. 136-162 Lieser,
  pp. 527-555 Friedlander,
  pp. 449-451

The elements 93 to 103, which do not occur in nature, together with protactium, thorium and uranium are members of the actinide group, whose electron shells differ by different filling of the 5f shell (analogous to the lanthanides, 4f). Transuranics can be produced by (multiple) neutron capture in reactors, by nuclear explosions or by heavy ion reactions.

The first transuranium, neptunium, was discovered in 1940 by McMillan and Abelson through the reaction.

$$^{238}_{92}U \quad (n,\gamma) \quad ^{239}_{92}U \xrightarrow[23{,}5\,\mathrm{min}]{\beta^-} {}^{239}_{93}Np \xrightarrow[2{,}3d]{\beta^-} {}^{239}_{94}Pu$$

Prepared and chemically isolated by co-precipitation on LaF_3. The genetic relationship of the new 2,3 d β-activity to the 23,5 min ^{239U} was demonstrated by milking (McMillan and Abelson, Phys.Rev. 57, 1985(1940)).

At first, it was not clear whether the 6d shell is further filled up in Np or the 5f shell. In the first case Np would be a homologous element of the VII subgroup. In the second case, it would be the fourth member of a newly discovered actinide series with a chemical behavior similar to uranium. The chemical properties of neptunium (rhenium-homologous or uranium-like) were elucidated by co-precipitation of carrier-free activities on inactive precipitates. Corresponding experiments are described below.

^{239}Np is prepared by irradiating ^{238}U with thermal neutrons (10 mg ^{238}U, 1 h at 100 kW, Φ = 7 * 1011 $cm^{-2}s^{-1}$) in the TRIGA reactor according to the above equation. The irradiated salt is dissolved in water: Np stock solution

1. **Preparation: Re-similar?**

   To 1 ml Np stock solution, 10 mg Ag^+ carrier and 10 ml H2O are added. Ag_2S is precipitated with H_2S water and a sample is prepared by filtration.

2. **Preparation: U-like?**

   To 1 ml of Np stock solution, add 10 mg of Th^{4+} carrier, 5 ml of 2N HCl, 5 ml of H_2O, and a spatula tip of $FeSO_4$. After cooling the solution, precipitate $Th(IO3)_4$ with an excess of KIO_3. If neptunium is an actinide element, it should be co-precipitated as $Np(IO3)_4$.
   Dispose Th containing residues in α-waste!

3. **Preparation: Re-similar?**

   To 1 ml Np stock solution add 5 mg Fe^{3+} carrier (50 drops), 10 ml 2N HNO_3 and a spatula tip $KBrO_3$. To achieve complete oxidation of the Np, boiling is required for 5 to 10 min (**fume hood - Br_2 formation!).** With carbonate-containing NH_3 solution in excess, $Fe(OH)_3$ is precipitated. If neptunium is an actinide element, it should remain in solution as a carbonate complex, analogous to uranium.

4. **Preparation: U-like?**

   To 1 ml of Np stock solution, add a heaped spatula tip of $NH_2OH \cdot HCl$ and 10 ml of H_2O. Boiling is carried out for 5 min. After addition of 5 mg Fe^{3+} carrier, $Fe(OH)_2$ is precipitated in the presence of SO_2 with carbonate-containing NH_3 solution. Neptunium should precipitate as hydroxide like uranium in the tetravalent state.

5. preparation: Re-similar?

To 1 ml Np stock solution, add 10 ml 2N HNO_3 and a spatula tip of $KBrO_3$. Boil in the fume hood for 5 to 10 min. After addition of 10 mg La^{3+} carrier and 5 drops of Zr^{4+} carrier, do a LaF_3 precipitation with saturated NaF solution.

LaF_3 precipitates slowly as a colorless solid only in an ice bath. As an actinide element, neptunium, which is in the form NpO_2^{2+}, should remain in solution, because for precipitation pure ions (Np^{6+}) would be necessary.

6. preparation: U-like?

To 1 ml Np stock solution add a heaped spatula tip of $NH_2OH \cdot HCl$ and 10 ml H_2O is added. It is boiled for 5 min. After addition of 10 mg of La^{3+}- and 5 drops of Zr^{4+}-carrier, LaF_3 is precipitated in the presence of SO_2 with saturated NaF solution. Neptunium should form a sparingly soluble fluoride in the tetravalent state, which is co-precipitated on the LaF_3 precipitate.

- **Standard preparation:**

A glass fiber filter, with a diameter equal to the inner diameter of the chimney of Hahn's Nutsche, is placed on a sample holder, soaked with 100 µl Np stock solution, dried under the radiant heater and covered with adhesive foil.

The oxidation and reduction of carrier-free neptunium proceeds very slowly. Therefore, the mentioned times for the individual experiments should be followed.

The samples are measured with a NaI(Tl) detector. The peak area of the 106 keV γ-line of the ^{239}Np is determined. No background correction is necessary. The count rates of samples 1 to 6 are referred to the count rate of the standard (100%). The following activity distribution is expected:

Table 1: Results of test day

Preparation	Precipitation	Neptunium activity %	Chemical behavior of neptunium
1	Ag_2S	1	No sulfide precipitation. No eka-rhenium
2	$Th(IO3)_4$	60	Co-precipitation as $Np(IO3)_4$
3	$Fe(OH)_3$	10	NpO_2^{2+} remains in solution as a carbonate complex like UO_2^{2+}
4	$Fe(OH)_2$	90	Co-precipitation as $Np(OH)_4$
5	LaF_3	10	NpO_2^{2+} remains in solution
6	LaF_3	100	Co-precipitation as NpF_4

Neptunium Chemistry

The samples are measured on the NaI detector (5 min each). The distance from the detector is determined by the assistant.

Pick up 1 ml of activity in the test tube and fill up to 10 ml = stock solution.

1. Add 3 drops of Ag^{+} carrier and 10 ml of H_2O to 1 ml of Np solution. Precipitate silver sulfide with H_2S water. Boil briefly (makes precipitate more filterable) and extract over membrane filter.

2. To 1 ml of Np solution, add 10 mg of Th^{4+} carrier, 5 ml of 2 N HCl, 5 ml of H_2O, and a spatula tip of iron(II) sulfate. Boil the solution for 5 min and cool well. In the cold, precipitate with KIO_3. The sample is later given to the α-waste.

3. Add 5 mg Fe^{3+} carrier (50 drops), 10 ml 2 N HNO_3 and a spatula tip of $KBrO_3$ to 1 ml Np solution. Oxidize in a fume hood by boiling for 5-10 min (Br_2 formation!). Precipitate iron(III) hydroxide with NH_3 containing CO_2. (If iron does not precipitate, the solution is still too acidic).

4. Add 10 ml H_2O and a heaping spatula tip of hydroxylamine to 1 ml Np solution and reduce in boiling heat for 5 min. Then add 5 mg Fe^{3+} and SO_2 water. Precipitate Fe(II) hydroxide with ammonia containing CO_2.

5. Add 10 ml of 2 N HNO_3 and a spatula tip of $KBrO_3$ to 1 ml of Np solution and oxidize in a fume hood for 5-10 min at boiling heat. Then add 10 mg of La^{3+} carrier and 5 drops of Zr^{4+} carrier and precipitate with saturated NaF solution. The precipitate is cooled with ice and extracted.

6. To 1 ml of Np solution, add 10 ml of H_2O and a heaped spatula tip of hydroxylamine. Reduce in the boiling heat for 5 min. Then add 10 mg of La^{3+} carrier and 5 drops of Zr^{4+} carrier, and SO_2 water. Then precipitate with saturated NaF solution. The precipitate is cooled in ice and extracted.

7. standard preparation (prepared by the assistant).

100 µl of the original solution was dried on a glass fiber filter with a diameter corresponding to the inner diameter of the vial. The preparation was then covered with adhesive tape.

Evaluation: The content of neptunium relative to the standard should be determined.

Disposal: The filtrates into the canisters, the precipitations into the β-short waste. The thorium preparation (experiment 2) into the α-waste.