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ELIMINATION OF INTERFERENCE BY NICKEL IN THE DETERMINATION OF URANIUM BY MEANS OF ZINC AMALGAM REDUCTORS

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ABSTRACT

The observation that zinc amalgam reductors are poisoned by solutions containing nickel is confirmed; experiments are described showing the effect in hydrochloric acid solutions. The effect is caused by deposition of metallic nickel on the amalgam surface, promoting vigorous evolution of hydrogen. This interference is easily overcome by using a solid amalgam richer in mercury than usual, thus lowering the activity of the zinc enough to prevent deposition of metallic nickel.

INTRODUCTION

Recent work by ~~J. B.~~ Heberling [1] has shown that the Jones Reductor quickly becomes "poisoned" by passage of solutions containing nickel through the reductor. Working with sulfuric acid solutions containing about 0.2 g of uranium and 0.04 g of nickel, Heberling concluded that only six to ten samples of comparable nickel content could safely be considered as having undergone 100% reduction in a standard reductor. He used a zinc reductor amalgamated with approximately 2% by weight of mercury. Because of this interference, it has heretofore been necessary to remove nickel as by electrolysis with a mercury cathode, or to reduce the uranium by shaking with a liquid zinc amalgam.

The work here reported was undertaken to overcome the poisoning difficulties, so that the convenient standard procedure using the Jones Reductor could be retained. The replacement of the 2% amalgam by a solid zinc amalgam containing approximately 10% by weight of mercury has overcome the poisoning difficulties.

EXPERIMENTAL

POISONING BY NICKEL IN HCl SOLUTIONS

The first experiments show that hydrochloric acid solutions containing nickel also poison the reductor. Seven solutions were made, each solution, 45 ml in volume,

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1/Heberling, J. B. A study of the effects of certain contaminants on the volumetric determination of uranium. Report A-1040, Section 2P.

containing 0.15 g of nickel, exactly 0.1117 g of iron, and 4.5 ml of HCl as the only acid. These were passed separately through the Jones Reductor (amalgamated with mercury so that the mercury was 3% of the total weight of amalgam). The solutions were titrated with 0.1 N $K_2Cr_2O_7$ using diphenylamine as internal indicator after the addition of phosphoric acid. Iron instead of Uranium was chosen here as the elements to be reduced because of certainty of the valence change after reduction. Table I gives the results obtained.

Re Poisoning of Jones Reductor by nickel in HCl solutions.

Table I

Solution No.	Taken	g Fe Found
1	0.1117 g Fe + 0.15 g Ni	0.1115
2	" "	0.1112
3	" "	0.1079
4	" "	0.1072
5	" "	0.1055
6	" "	0.1047
7	0.0279 g Fe + 0.15 g Ni	0.0275

The results show that the reductor becomes poisoned after about 0.3 g of nickel is passed through, and that this poisoning occurs in hydrochloric acid solutions, as well as in the sulfuric acid solutions studied by Heberling. Solution No. 7 indicate that more nearly 100% reduction is obtained for smaller quantities of iron. This is to be expected because there is a larger area of zinc per weight of iron. As observed by Heberling in sulfuric acid solutions, metallic nickel was deposited, darkened the reductor, and somehow promoted the evolution of hydrogen. The evolution of hydrogen was so vigorous that after solution No. 7 had been passed through the reductor, it was almost impossible to get another sample through the reductor. This vigorous evolution of hydrogen probably interferes with the proper contact of the solution with the zinc amalgam.

NON-POISONING OF THE "10%" JONES REDUCTOR IN SULFURIC ACID SOLUTIONS lc

It was found that amalgamating the zinc with 10% by weight of mercury reduced its activity sufficiently so that no nickel plated out in the reductor and the poisoning difficulties were eliminated.

Solutions were prepared, each having a total volume of 45 ml, containing 0.15 g Ni and 0.1561 g U (average of three standardizations) and 10% by volume of sulfuric acid. The solutions were passed through the ~~Z~~ "10%" reductor, whose preparation is described in a later section, at the rate of about 40 mlsper minute and were washed with 3% H_2SO_4 and then with enough water so that the final acid concentration after reduction was about 4% by volume H_2SO_4. The solutions were then aerated for five minutes, because the color of the solution indicated the presence of trivalent uranium, and then were titrated with standard potassium permanganate solution (0.02980 N). The results are given in Table II.

Non-poisoning of "10%" Reductor in H_2SO_4 solutions by nickel

Table II

	Taken		U g found
1	0.1561 g U	+ 0.15 g Ni	0.1561
2	"	"	N T*
3	"	"	0.1561
4	"	"	N T*
5	"	"	0.1561
6	"	"	N T*
7	"	"	0.1562
8	"	"	N T*
9	"	"	0.1560
10	"	"	N T*
11	"	"	0.1560
12	"	"	N T*
13	"	"	0.1561
14	"	"	N T*
15	"	"	0.1561
16	"	"	N T*
17	"	"	N T*
18	"	"	0.1562
19	"	"	N T*
20	"	"	N T*
21	"	"	0.1561
22	"	"	N T*
23	"	"	N T*
24	"	"	0.1560
25	"	"	N T*
26	"	"	N T*
27	"	"	0.1562
28	"	"	N T*
29	"	"	N T*
30	"	"	0.1562
31	"	"	N T*
32	"	"	N T*
33	"	"	0.1561
34	"	"	0.1561

* N T = not titrated

The results show that the reductor was not poisoned even after more than 5 g of nickel had passed through it. This corresponds to over 100 samples of the kind of uranium ore normally dealt with. It must be noted also that the amount of nickel used in each experiment was at least three times the amount usually found and that even with these amounts no poisoning of the reductor ensued. No gas evolution was observed even with sample No. 34. After the experiments the reductor looked like new.

To see if any nickel had actually plated out on the reductor, the top one inch of amalgam was removed and dissolved in aqua regia. A qualitative test with dimethylglyoxime showed no nickel.

NON-POISONING OF THE "10%" JONES REDUCTOR IN HYDROCHLORIC ACID SOLUTIONS lc

The "10%" Jones Reductor was further tested on solution containing hydrochloric acid as the only acid. Eleven test samples were made up of each containing exactly 0.1117 g Fe, 0.15 g Ni, and 4.5 ml HCl in a total volume of 45 ml. These solutions were reduced with the "10%" reductor and titrated as before. Again no poisoning resulted as shown in Table III.

Non-poisoning of the "10%" Reductor by nickel in HCl solutions

Table III

Solution No.	Taken	g Fe Found
1,2,3,4,5,6,7	0.1117 g Fe + 0.15 g Ni	N T*
8	" "	0.1117
9	" "	0.1118
10	" "	0.1117
11	" "	0.1117

* N T = not titrated

BEHAVIOR OF VANADIUM, TITANIUM AND MOLYBDENUM ON REDUCTION IN THE "10%" JONES REDUCTOR lc

Tests made on sulfuric acid solutions showed that the 10% Jones Reductor reduces vanadium to the divalent state, titanium to the trivalent state and molybdenum to the trivalent state. These valence states are identical with those obtained by use of a standard Jones reductor so that these elements may be determined by the usual procedures with a "10%" Jones Reductor.

PREPARATION OF THE "10%" JONES REDUCTOR /c

A. Preparation of the "10%" amalgam

Dissolve 23.6 g of $HgCl_2$ in 400 ml of water containing about 10 ml of nitric acid. Transfer the solution to a 500 ml separatory funnel. Add 180 g of 20 mesh zinc and immediately shake. Shake for about 2 minutes, releasing any gas pressure from time to time. Wash the amalgam with dilute sulfuric acid and then wash thoroughly with water.

B. Preparation of the reductor column

The reductor used for all tests described had an inside diameter of 11 mm and was filled with 12 1/2 inches of zinc amalgam. To prepare, first add a little water to the tube and then introduce about an inch of the amalgam at a time, gently tamping it in place with a glass rod.

CONCLUSIONS

A Jones Reductor containing zinc amalgamated with 10% mercury does not become poisoned by passage of nickel bearing solutions through the reductor. Either hydrochloric acid or sulfuric acid solutions may be used. The valence changes during reduction of the elements commonly determined by means of the Jones Reductor are the same for the "10%" reductor and the standard reductor.