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SEPARATION OF U AND Pu FROM Zr, Nb, Ru AND Cs ON A COLUMN OF MANGANESE DIOXIDE.

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by

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Abstract

The adsorption of U, Pu, Zr, Nb, Ru, Sr-Y and Cs was examined to provide a good separation of uranium and plutonium from the fission products mentioned.

It was established that it is quantitatively possible to wash UO_2^{++} and PuO_2^{++} from a column of manganese dioxide with 0.1 N HNO_3. Under the same conditions, 99.2% of Zr^{95}, Nb^{95}, Ru^{106} and Cs^{137} was adsorbed.

Introduction

In the aqueous process for the separation of uranium and plutonium from fission products, the most difficult problem is the separation of Zr, Nb, and Ru(1,2). Because of these difficulties, it is very often necessary to add special steps to a process in order to get a good decontamination from these three elements. Final decontamination of U(3) and Pu(2) from Zr and Nb is obtained by passing the acid solution over a column of silica gel.

Culler(4) used co-precipitation of fission products with manganese dioxide as a preliminary decontamination prior to solvent extraction in reprocessing highly active fuels. Potassium permanganate is added to the feed solution, which is heated, and permanganate is reduced to manganese dioxide. Permanganate and manganese dioxide both oxidize plutonium to PuO_2^{++}. PuO_2^{++} does not adsorb on manganese dioxide. Harmon(5) described a preliminary separation of Ru, Zr and Nb prior to solvent extraction by using potassium permanganate for the oxidation of ruthenium to the volatile tetroxide, which is distilled off from the feed solution. On the other hand, the use of permanganate results in formation of manganese dioxide, which can be used for the removal of Zr and Nb.

It is probable that this process is not the most convenient because of the necessity of separating the precipitate by centrifuging, which is very inconvenient in large-scale experiments and in continuous processing.

The purpose of this work was the examination of the adsorption of U, Pu, Zr, Nb, Ru and some other fission products of interest to the reprocessing and to provide an adequate separation of plutonium and uranium from fission products on a column of manganese dioxide.

Experimental procedure

1. Preparation of manganese dioxide

One of the methods for the preparation of manganese dioxide is to treat potassium permanganate solution with a solution of a manganous salt (6,7) by the reaction:

$$3\ Mn^{++} + 2\ MnO_4^- + 2\ H_2O \rightarrow 5\ MnO_2 + 4H^+$$

G. Forschhammer (6) used a mixture of 2 moles of potassium permanganate and 3 moles of the manganous salt in a dilute solution. A.P. Lunt (7) used a mixture of 400 ml of a saturated solution of potassium permanganate and 400 ml of a saturated solution of manganese sulphate.

In this work, manganese dioxide was prepared by the gradual addition of the solution of manganous sulphate (101.4 gr of $MnSO_4 \cdot H_2O$ in 1 l H_2O) to a solution of the permanganate (63,2 g $KMnO_4$ in 5 l H_2O). After filtration the precipitate was washed with hot water till free from acid, then with 1 l of 3 N HNO_3 and again with water till free from acid. The precipitate was dried for about 20 hours at 110°C. The prepared manganese dioxide was boiled for 5 minutes in 3 N HNO_3 and boiling stopped by the addition of cold distilled water. The precipitate was washed with distilled water until the filtrate was free from acid and then dried for about 80 hours at 110°C. The prepared manganese dioxide was first sieved, and the fraction from 100-140 mesh was used. This fraction contains small amounts of a very fine powder of manganese dioxide easily removable by decantation in water.

2. X-Ray Analysis of Manganese Dioxide

X-ray diagrams were taken with Cu and Mo-irradiation. Only 3-4 faint and diffuse lines were found, indicating that the substance consisted of rather small crystallites (nearly X-ray amorphous). By comparison with the ASTM card index (no. 4-0779), the lattice was identified as γ-MnO_2.

3. Preparation of the Column of Manganese Dioxide

Manganese dioxide (100-140 mesh) was made into a slurry with water and the fine powder removed by decantation. Then it was poured into a 2 mls column. The column was then washed with 50 mls of 1 N HNO_3 and afterwards with distilled water.

4. Procedure

On the column of manganese dioxide, prepared as described above, solutions of UO_2^{++}, PuO_2^{++}, Pu (IV), Zr^{95} - Nb^{95}, Ru^{106}, Sr^{90}-Y^{90}, Cs^{137}-Ba^{137} were adsorbed separately, and the column washed with HNO_3 in different concentrations.

After washing the column, the quantity of the element in the effluent as well as the quantity adsorbed on the manganese dioxide was determined. In the case of U^{233} and Pu^{239}, only the effluent was analyzed. To determine the quantity of adsorbed element on the column, manganese dioxide was dissolved in dilute HNO_3 containing sodium nitrite, hydroxylamine or hydrogen peroxide, and the solution diluted to a desired volume. Beta and gamma activity were recorded from an aliquot of 0.5-2 mls and alpha activity from an aliquot of 50-100 λ. Alpha activity was measured with a scintillation counter of conventioned type (ZnS screen on the photocathode of an E.M.J. photomultiplier tube) and Beta activity was measured with an ordinary type Philips Geiger-Müller counter.

U^{233} is prepared in the Isotope Department at this Institute.

Pu^{239} was purified by the extraction with 0,2 M TTA (Thenoyltrifluoroacetone) in CCl_4 (8).

The solution of Pu (VI) was prepared using freshly precipitated silver peroxide (9) as oxidizing agent.

Pu (IV) was prepared by evaporating the solution of Pu with nitric acid in the presence of hydrogen peroxide or perchloric acid. This operation was repeated and the residue was dissolved in nitric acid (in this case sodium nitrite could not be used because of the dissolution of MnO_2 in the presence of nitrite). The solution of Zr^{95} - Nb^{95} in 0,5% Oxalic acid (Received from Radiochemical Center, Amersham, England) was treated with conc. nitric acid in the presence of some drops of perchloric acid. The solution was evaporated to dryness to destroy oxalic acid. The operation was repeated several time, at the end the evaporation was carried out with conc. nitric acid. The residue was disolved in 5 N nitric acid. From this solution, the solutions in 0,1 and 1 N nitric acid were prepared by dilution with water.

Ru^{106} was in 8 N nitric acid (Received from Radiochemical Center, Amersham, England). The solutions of Ru^{106} in 0,1, 0,5 and 1 N nitric acid were prepared by dilution the original solution with water.

Sr^{90} and Cs^{137} are separated from a mixture of fission products (10,11).

5. Results

The solution of U^{238}(VI), U^{233}(VI) and Pu^{239}(VI) from 0.001 N HNO_3 (100-200 λ aliquot) was adsorbed on the column of manganese dioxide. The column was washed with 0.1, 0.5 and 1 N HNO_3. The elution curves for U^{233} (VI) and Pu^{239} (VI) are given in figures 1 and 2. U^{233} (VI) and Pu^{239} (VI) both are quantitatively eluted.

The experimental data for U (VI), Pu (VI), Zr^{95}-Nb^{95}, Ru^{106}, Sr^{90}-Y^{90} and Cs^{137}-Ba^{137} are given in Table I.

After these experiments, 25 mls of a solution of uranium containing 12.9 g U/ml in 0.1 N HNO_3 was passed through a column, and the column washed with 10 mls of 1 N HNO_3. No Beta or Gamma activity could be detected in the effluent, which means that UX was adsorbed on the column under the conditions mentioned.

At least 25 mls of a solution of UO_2^{++}, Zr^{95}-Nb^{95}, Ru^{106} and Cs^{137} in 0.1 N HNO_3 was passed through a column. After that, the column was washed first with 0.1 N HNO_3 and then with 50 mls 1 N HNO_3. The experimental data are given in Table II.

6. Capacity Determination of Manganese Dioxide for Zr

Zirconium nitrate was dissolved in 4 N HNO_3 and diluted to 1 N HNO_3. Capacity determinations were carried out by passing about thirty times the amount of Zr necessary to saturate manganese dioxide through a column, washing the column with 50 mls of 1 N HNO_3 and dissolving manganese dioxide in dilute nitric acid plus hydrogen peroxide. Zirconium was determined gravimetrically as ZrP_2O_7 (12).

The obtained value for the capacity was 24 ± 1 mg/g MnO_2, dried at 110°C.

Discussion

From the results given in Tables I and II, it is seen that Zr^{95}-Nb^{95}, Ru^{106} and Cs^{137} are adsorbed on the column of manganese dioxide and that by using such a column of manganese dioxide, it is possible to separate them from U (VI) and Pu (VI) in a solution of 0.1 N HNO_3.

Separation of uranium from these elements is simple to carry out. When Pu is also present in solution, it is necessary to have an oxidizing agent present to provide PuO_2^{++}; but under these conditions it is probable that some Ru is oxidized to the volatile RuO_4. Perhaps it would be convenient to carry out the oxidation of Pu under conditions similar to the Redox process (4), using $KMnO_4$ or MnO_2 as oxidising agent, or to oxidise Pu at room temperature with silver peroxide or with $S_2O_8^{--}Ag^+$.

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TABLE I

Element Present		Amount of Eluate	Amount of Element Present in Effluent, in %		
U^{233} (VI)	~ 2,5 μg	20 ml 0.1 N HNO_3	99.5		*
U^{233} (VI)	~ 2,5 μg	10 ml 1 N HNO_3	98.4		*
Pu^{239} (VI)	~ 0,6 μg	20 ml 0.1 N HNO_3	98.8		*
Pu (VI)	~ 0,6 μg	10 ml 1 N HNO_3	100.5		*
Pu (IV)	~ 0,5 μg	22 ml 1 N HNO_3	43		x
Pu (IV)	~ 0,6 μg	10 ml 5 N HNO_3	42.8		x
Zr^{95}-Nb^{95}	$6.33 \cdot 10^5$ cpm	10 ml 1 N HNO_3	~ 0.02		o
		+ 10 ml 1 N HNO_3	—		
		+ 25 ml 5 N HNO_3	~ 0.06		
		30 ml conc. HNO_3	69.6		
Zr^{95}-Nb^{95}	$6.30 \cdot 10^5$ cpm	10 ml 1 N HNO_3	0.07		x
Ru^{106}	$5.51 \cdot 10^5$ cpm	10 ml 0.1 N HNO_3	0.26		*
		+ 10 ml 0.5 N HNO_3	~ 0.05		
		+ 10 ml 1 N HNO_3	0.5		
		+ 10 ml 5 N HNO_3	17		
Ru^{106}	$5.41 \cdot 10^5$ cpm	10 ml 0.5 N HNO_3	3.5		o
		+ 10 ml 0.5 N HNO_3	~ 0.08		
		+ 10 ml 1 N HNO_3	~ 0.09		
		+ 10 ml 5 N HNO_3	6.9		
Sr^{90}- Y^{90}	$5 \cdot 10^5$ cpm	10 ml 0.1 N HNO_3	45.4	mostly Sr^{90}	o
		+ 10 ml 0.1 N HNO_3	0.6		
		+ 10 ml 1 N HNO_3	56	mostly Y^{90}	
Cs^{137}-Ba^{137}	$4.12 \cdot 10^5$ cpm	10 ml 0.1 N HNO_3	—		o
		+ 20 ml 1 N HNO_3	—		
		+ 10 ml 5 N HNO_3	—		
Ru^{106} (treated with $(NH_4)_2$, S_2O_8 and Ag NO_3 at room temperature)	$5.4 \cdot 10^5$ cpm	10 ml 1 N HNO_3	2.7		*

TABLE I continued

The column volume of manganese dioxide was 2 mls and the flow rate was 3 mls/min/cm^2.

(*) The column of manganese dioxide was prepared as previously described, washed with 50 mls of 1 N HNO_3 and then with water until the effluent was free from acid.

(x) The column of manganese dioxide was pre-treated with 1 N HNO_3.

(o) The column was pre-treated with 0.1 N HNO_3.

TABLE II

Element Present in 25 mls	Amount Eluate	Beta Activity in the Effluent in %
U 0.3237 gr		
Zr^{95}-Nb^{95} 841.700 cpm	25 ml 0.1 N HNO_3	0.8
Ru^{106} 2.164.800 cpm		
Cs^{127} 130.560 cpm	+ 50 ml 1 N HNO_3	3.7

FIGURE I.

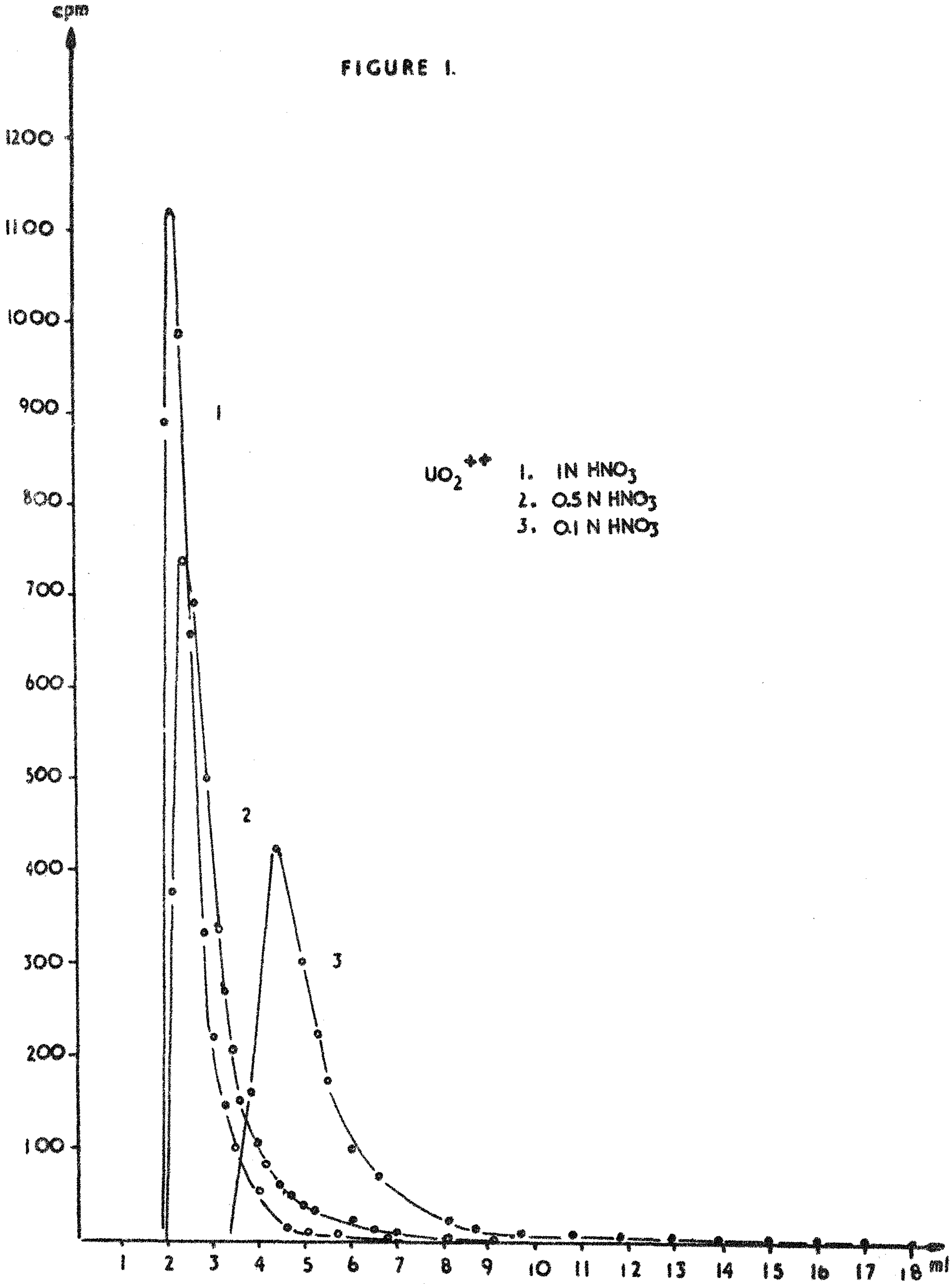
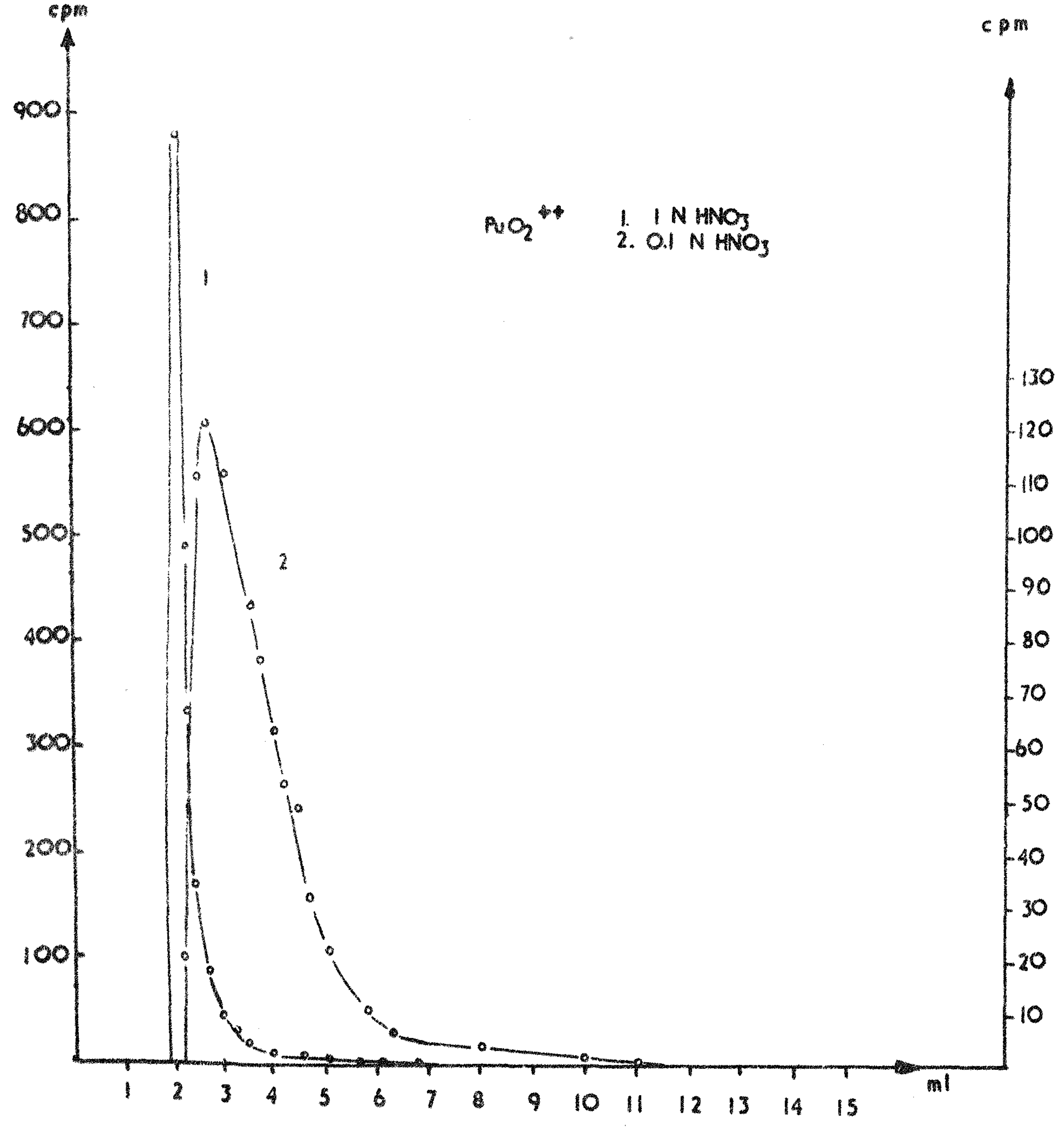

cpm
1200
1100
1000
900
800
700
600
500
400
300
200
100
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
ml
1
2
3
UO_2^{++}
1. 1N HNO_3
2. 0.5 N HNO_3
3. 0.1 N HNO_3

FIGURE 2.



cpm
900
800
700
600
500
400
300
200
100
cpm
130
120
110
100
90
80
70
60
50
40
30
20
10
PuO_2^{++}
1. 1 N HNO_3
2. 0.1 N HNO_3
1
2
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
ml