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Adsorption of Certain Radioactive Colloids on Glass

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Adsorption of Certain Radioactive Colloids on Glass

By

Stephen Charles Carniglia
B.S. (University of California) 1943

THESIS

Submitted in partial satisfaction of the requirements for the degree of

MASTER OF SCIENCE

in

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ADSORPTION OF PLUTONIUM ON GLASS

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III. Nature of the Adsorption Process

I. INTRODUCTION

As an alpha-emitting radioelement, plutonium^{239} lends itself conveniently to microchemical investigations at high dilution, its detection and estimation being made by the common radioactive tracer techniques. However, the extremely small quantities employed in tracer studies give rise to problems not encountered in work at higher concentrations. One of these, analytical in nature, is the adsorption of one form of this element out of aqueous solutions by glass surfaces. This phenomenon may interfere seriously with any quantitative work involving transfer from one item of glassware to another, for example pipetting, diluting, and transferring aliquots for analysis. Thus this problem has been primarily a practical one, involving the determination of the states of plutonium which are subject to adsorption by glass, and of the conditions under which adsorption will or will not take place.

At the time these investigations were made, four oxidation states of plutonium in aqueous solution were known, +3, +4, +5, and +6. It had been determined that one form of the +4 state behaved similarly to other quadrivalent ions, while another form showed some distinctly abnormal characteristics (a), (b),(c),(d). This "abnormal" form had been studied to some extent, and it had come to be recognized as a colloidal hydrolytic product of the "normal" +4 ion, presumably a hydrous oxide or hydroxide or perhaps a basic salt (d),(e),(f),(g),(h). (In this respect the +4 state of plutonium is not unusual. Such ions as ceric, uranous, zirconyl, and thorium can be made to undergo hydrolysis and formation of a colloidal dispersion under proper conditions of metal-ion concentration, acidity, and temperature. Indeed, colloidal sols of most slightly soluble metal oxides or hydroxides have been prepared.)

This colloidal substance was suspected to be the offender with respect to glass adsorption, as well as to the other extraordinary behavior observed. King (i),(j) had made some preliminary investigations of this problem at very high dilution, but his findings were inconclusive.

Since it is not the intent of this paper to imply the exact forms in which the several states of plutonium exist in aqueous solution, the notation which has been generally used in this work will be followed here. That is, the +4 oxidation state will be referred to as Pu(IV), the +6 as Pu(VI), etc., whereas the ionic species predominating in solution are probably Pu^{+4} and PuO_2^{++}, respectively. Similarly the colloidal hydrous oxide, hydroxide, or basic salt of Pu(IV) will be referred to as "colloidal Pu(IV)", since its exact composition is not known. With regard to concentrations the term "formal", or "f", will be used, since colloidal particles are of indefinite molecular weight. The most probable formulas ($PuO_2 \cdot xH_2O$, $Pu(OH)_4 \cdot xH_2O$, $PuOX_2 \cdot xH_2O$) contain only one metal atom; thus a 0.001 f sol contains 0.001 mole of Pu atoms, or 0.239 gram of plutonium, per liter.

It is not necessary to describe here the preparation of solutions of the various states of plutonium. Standardized methods have been employed, and purity of state as determined from absorption spectra (k),(l) has been found quite sufficient for this work. Preparation of the colloidal Pu(IV) sols used may be of interest, however, as will also their absorption spectra.

Hydrolysis occurs upon allowing a dilute acid solution (i.e., about 0.1 M in H^+) of a Pu(IV) salt to stand for several days, or quite rapidly upon heating such a solution to 100°C (a),(d),(f),(m),(n),(o). Repeated precipitation of the hydroxide followed by dissolving (or rather, peptising) in a minimum of acid at 70°-100°C seems most effective in obtaining the highest percentage of the Pu(IV) in the colloidal state(b). In a typical example five precipitations with excess dilute NaOH were performed; the last precipitate, containing 0.065 millimole of plutonium, was peptised in 1.8 ml of 0.33 M HCl. The sol was diluted with 33 ml of 0.15 M HCl to give a product 35 ml in volume, 0.0018 f in Pu, and 0.153 M in HCl.

The absorption spectrum of this sol was obtained with a Beckman photoelectric spectophotometer. In Fig. I is plotted the resultant curve of molal extinction coefficient[1] versus

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[1] The molal extinction coefficient for colloidal Pu(IV) sols might better be called the "formal" extinction coefficient. It is obtained from the measured log I_0/I by the relation,

$$\epsilon = \frac{\log I_0/I}{l \cdot c},$$

where l is the path length in centimeters and c is the concentration of Pu in formula weights (of $Pu(OH)_4$, for example) per liter.

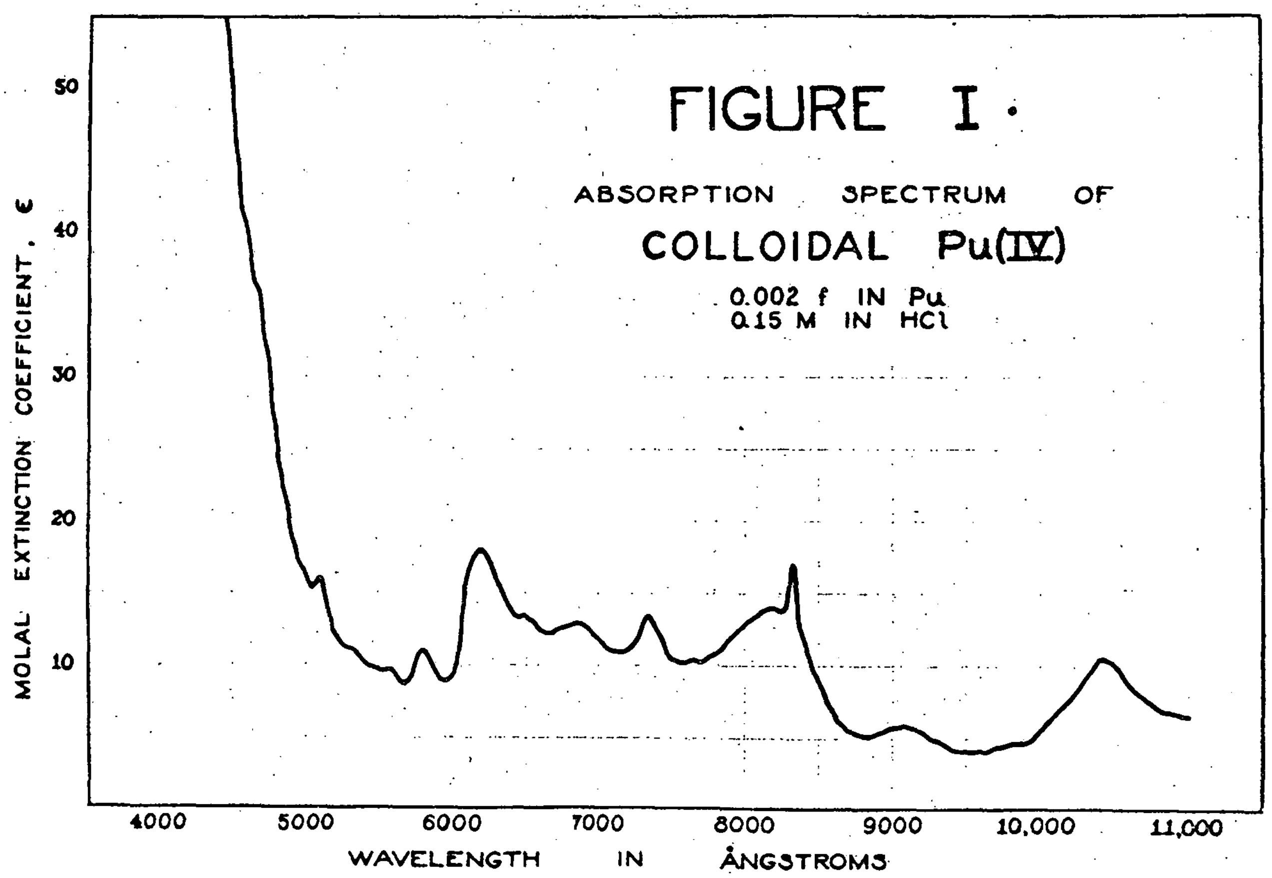

FIGURE I.

ABSORPTION SPECTRUM OF COLLOIDAL Pu(IV)

0.002 f IN Pu
0.15 M IN HCl

wavelength. Distinguishing features of this curve are the absorption maxima at 5300 Å, 6200 Å, and 7350 Å, the high general absorption, and the steep rise in absorption with decreasing wavelength beginning at about 5300 Å. These features remain after correction of the curve for the presence of all other forms of plutonium, and thus they serve to identify colloidal Pu(IV). General absorption (and consequently the value of ϵ at any point) seems to depend upon preparation and treatment of the sol; therefore estimation of colloidal Pu(IV) by measurement of its absorption maxima may be subject to errors as high as 20%. (For other absorption spectra which have been recorded for this substance, see the following references: (p),(q),(r).)

Comparison of Fig. I with the absorption spectra of the other states of plutonium (k),(l) shows that this sol contained less than 10% of Pu(III), ionic Pu(IV), and Pu(VI) combined, even though dialysis was not attempted. No effort was made to achieve higher purity, as the presence of the other states does not interfere with interpretation of the experimental results.

Lastly, before beginning the discussion of the experimental work, it is desired to deal with the question of the +5 state of plutonium. At the time this work was done the conditions favoring existence of this ion at moderate concentrations were not known. Its absorption maxima are too low to permit detection of 10% Pu(V) in the solutions employed here (l); therefore the curves obtained in this work give no indications of its presence or absence. More recently it has become possible to prepare stable solutions as high as 50% in Pu(V), and an investigation of this state is indicated. However, this paper will be concerned with only the +3, +4, and +6 states.

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II. THE PRACTICAL PROBLEM:

CONDITIONS UNDER WHICH ADSORPTION OCCURS

In the investigations of sections A, B, and C below, the extent of adsorption by glass was tested in the following way: 3 to 5 μg of plutonium (in 0.5 to 1.0 μl of dilute acid) was delivered into a one milliliter Pyrex centrifuge cone containing 0.5 ml of a chosen medium. (The area of glass in contact with the solution was approximately 5 cm^2.) The system was well stirred, and then allowed to stand a measured length of time with occasional stirring. The entire solution was then mounted on a platinum dish for counting of its alpha activity, while the remainder of the plutonium was leached from the walls of the cone and estimated either by direct mount or by the lanthanum fluoride analysis technique (3).

Completeness of recovery was checked occasionally by finally breaking up the cone in which an adsorption experiment had been run and counting a representative group of the fragments for alpha activity. In nearly all cases, less than one per cent of the total activity was found on the glass after the leaching operations.

A. Adsorption of Pu(III) and Pu(VI): These states are not appreciably adsorbed except at low acidity. Data are given in Tables I and II.

It is quite possible that even the adsorption occurring at pH values above 1 may be due to traces of Pu(IV) in these solu-

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TABLE I

Adsorption of Pu(III) by Glass

Volume — 0.5 ml   Area of Glass Surface — 5 cm²

Room Temperature

Medium	Time of Contact	Total Pu(III) Present (micrograms)	% Adsorbed
0.05 M H_2SO_4	2 hrs.	3.64	0.12
0.1 M HNO_3	"	3.43	0.2 - 0.5
0.1 M KCl	"	3.01	0.14
0.1 M HCl	"	3.70	0.20
10^{-2} M HCl	"	3.62	1.1
10^{-3} M HCl	"	3.20	3.0
10^{-4} M HCl	"	3.62	7.5
10^{-5} M HCl	"	3.03	7.4

TABLE II

Adsorption of Pu(VI) by Glass

Volume — 0.5 ml   Area of Glass Surface — 5 cm²

Room Temperature

Medium	Time of Contact	Total Pu(VI) Present (micrograms)	% Adsorbed
0.1 M HNO_3	3 hrs.	3.35	0.26
0.1 M HNO_3, trace $K_2Cr_2O_7$	3 hrs.	2.61	0.18
0.1 M HNO_3, 0.03 M $K_2Cr_2O_7$	3 hrs.	3.39	0.05
10^{-2} M HNO_3	2.5 hrs.	4.46	6.3
10^{-3} M HNO_3	"	3.53	11.0
10^{-4} M HNO_3	"	3.52	12.3
10^{-5} M HNO_3	"	3.66	12.0

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tions or to impurities capable of oxidizing or reducing small quantities of the other states to Pu(IV). At low acidity this ion would probably hydrolyze rather rapidly, the product being adsorbed (see section C below). In support of this the low adsorption from the Pu(VI) solution in the presence of $Cr_2O_7^{--}$ at pH = 1 is pointed out (Table II); experiments of this kind at lower acidity are indicated.

B. Adsorption of the Ionic Species of Pu(IV) — the "Normal" Form: Due to the fact that hydrolysis sets in at low acidity, no comparison of adsorption with pH is possible for this ion. However, several "normal" Pu(IV) salt solutions were prepared and tested for adsorption in 0.1 M acid. Adsorption ranged from 2% to 5%, apparently depending upon the care exercised in destroying traces of colloidal material in the preparation of the solutions.

C. Adsorption of Colloidal Pu(IV): In these studies small quantities of a colloidal Pu(IV) sol were introduced into a variety of dilution media. Thus in addition to the mere measurement of adsorption from dilute acid solutions an attempt was made to detect any effect due to acidity, oxidizing or reducing agents, or complexing anions. The results are shown in Table III, and discussed in section F below.

D. Removal of Adsorbed Material: The colloidal Pu(IV) which adhered to the cone walls showed a marked resistance to

[illegible]

TABLE III

Adsorption of Colloidal Pu(IV) by Glass

Volume — 0.5 ml   Area of Glass Surface — 5 cm²

Medium	Time of Contact and Temperature	Total Pu(IV) Present (ug)	% Adsorbed
0.1 M HNO_3	0.5 hr. at room temp.	2.34	67.
"	" "	3.95	63.
"	4 hrs. at room temp.	4.09	51.
"	22 hrs. at room temp.	4.09	56.
"	22 hrs. at r.t., then 1 hr. at 95°C.	4.09	70.
0.5 M HNO_3	4 hrs. at room temp.	3.95	36.
"	" "	3.95	47.
5.0 M HNO_3	0.5 hr. at room temp.	2.34	40.
10. M HNO_3	" "	2.34	25.
"	" "	3.95	40.
12. M HCl	0.5 hr. at room temp.	3.97	27.
0.1 M H_2SO_4	5 hrs. at room temp.	3.97	26.
1.0 M H_2SO_4	" "	4.07	17.
10. M H_2SO_4	" "	3.97	3.
36. M H_2SO_4	" "	3.97	0.5
0.5 M Na_2SO_4, 0.02 M HNO_3	5 hrs. at room temp.	3.41	26.
0.5 M Na_2SO_4, 0.1 M HNO_3	" "	3.75	8.5
0.5 M Na_2SO_4, 1.0 M HNO_3	" "	3.73	5.6
0.5 M Na_2SO_4, 8.0 M HNO_3	" "	3.39	2.3
2.0 M HF, 0.67 M HNO_3	4 hrs. at room temp.	3.77	0.2
1.0 M NH_4OH	74 hrs. at room temp.	3.72	21.
0.3 M $(NH_4)_2C_2O_4$	4.5 hrs. at r.t.	3.53	8.0
"	" "	3.53	9.3
0.5 M HNO_3, 0.5 M SO_2	0.25hr. at room temp.	4.02	31.
"	0.5 hr. at room temp.	4.02	27.
"	1.0 hr. at room temp.	4.02	25.
"	1.5hrs. at room temp.	4.02	20.
"	1.5 hrs. at r.t., then 1 hr. at 75°C	4.02	9.
0.05 M HNO_3, 0.05 M $K_2Cr_2O_7$	1 hr. at 95°C, then 1 hr. at r.t.	3.60	47.
"	" "	3.71	49.

leaching agents. Concentrated HNO_3 was ineffective unless hot: a single wash of 16 M HNO_3 removed 25% of the adsorbed material upon 3 minutes contact at room temperature, as compared with 90 to 95% removed by a similar wash heated to 95°C for 3 minutes. Concentrated sulfuric acid was quite effective. Reduction by SO_2 and by $HONH_2 \cdot HCl$, and oxidation by $Cr_2O_7^{--}$, all proved unsatisfactory even when hot. A 3 M HF wash, or HF employed in a lanthanum fluoride precipitation, gave excellent results if allowed to stand in contact with the glass for 10 minutes. Thus, 99% or more of the adsorbed Pu(IV) was leached from the glass cone by a single treatment.

E. Saturation of the Glass Surface: In one series of experiments varying amounts of Pu(IV), as a colloidal sol, were introduced into one milliliter Pyrex centrifuge cones containing in every case 0.5 ml of 0.1 M HNO_3. The liquid and glass were analyzed separately for plutonium as before; results are shown in Table IV and plotted in Fig. II. It is seen that saturation of the glass surface occurs at about three times the concentrations of Pu(IV) employed in the experiments discussed above (Section II-C). The nearness of the former concentrations to the saturation level evidently did not influence the extent of adsorption from those solutions, however, as the highest per cent adsorption often occurred in this near-critical region.

F. Conclusions: At 0.1 M acid or higher, Pu(III), Pu(VI), and the ionic species of Pu(IV) are not adsorbed by glass.

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TABLE IV

Glass Adsorption as a Function of Colloidal Pu(IV) Concentration

Volume -- 0.8 ml
Medium -- 0.1 M HNO_3

Area of Glass Surface -- 5 cm^2
Room Temperature

Total Pu(IV) Present (micrograms)	Time of Contact	% Adsorbed	Micrograms Adsorbed
0.034	3.5 hrs.	60.	0.020
0.036	"	44.	0.016
0.19	3.5 hrs.	35.	0.064
0.23	"	26.	0.060
0.39	5.0 hrs.	37.	0.14
0.42	"	35.	0.15
0.96	3.5 hrs.	32.	0.31
0.98	"	41.	0.40
3.23[2]	5.0 hrs.	53.	1.71
3.49[2]	"	65.	2.27
8.7	6 hrs.	32.	2.78
9.1	"	38.	3.46
89.	6 hrs.	5.4	4.81
89.	"	5.4	4.81

[2] The ratio of glass surface area to quantity of plutonium in these two experiments is the same as that in the experiments of Tables I, II, and III.

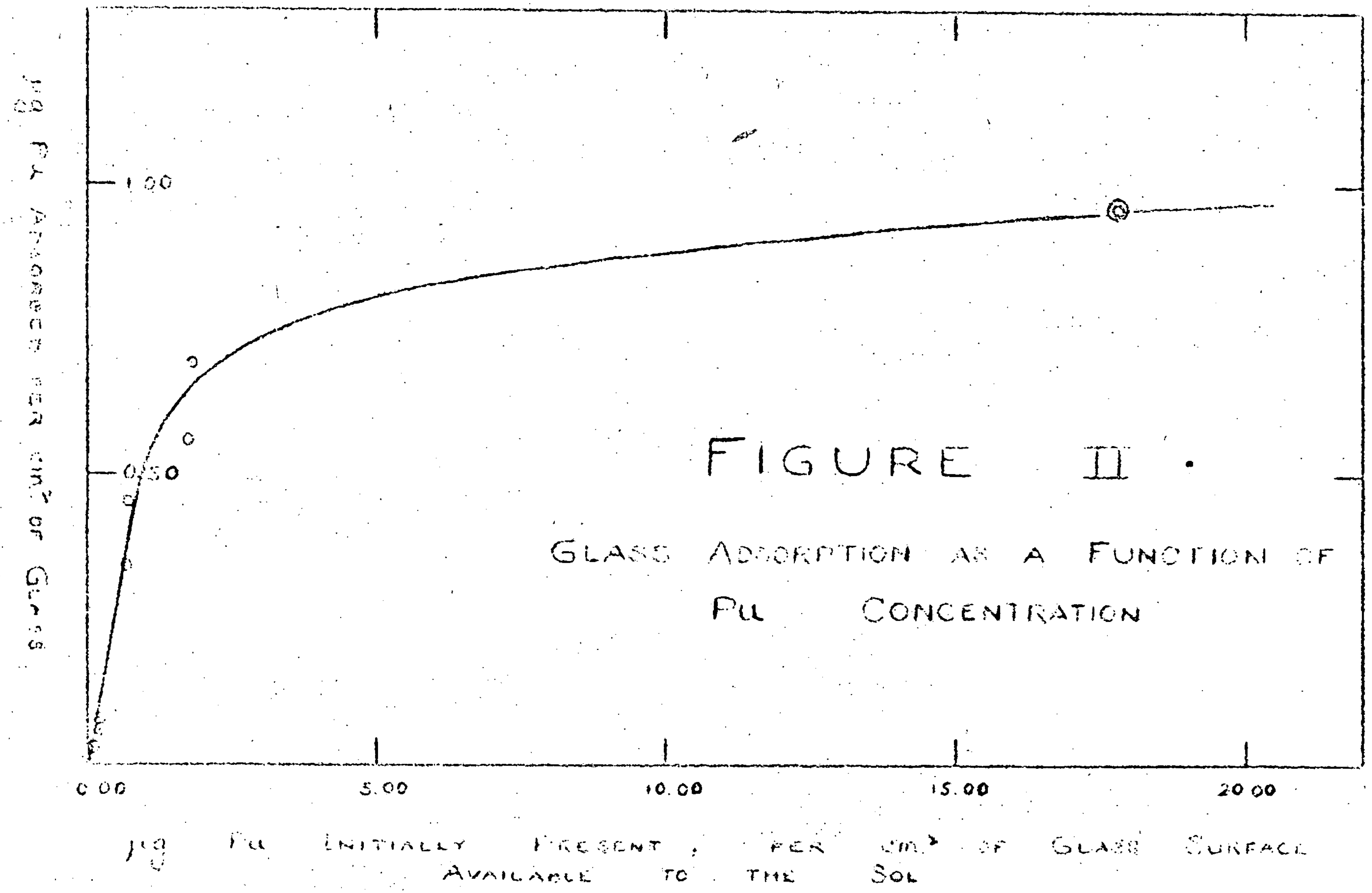

FIGURE II.

GLASS ADSORPTION AS A FUNCTION OF Pu CONCENTRATION

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Colloidal Pu(IV) is extensively adsorbed, for example about 50% being common in 0.1 M acid. Adsorption drops off slowly with increased acid concentration, HCl and HNO_3 being quite comparable. Sulfuric and hydrofluoric acids and ammonium oxalate exert a marked effect, due undoubtedly to the very great stability of the sulfate, fluoride, and oxalate complexes of the +4 state(t),(u). Effects of other substances can be detected but are of a lesser magnitude, SO_2 as a reducing agent modifying the extent of adsorption noticeably in time.

There is no evidence of a time-dependence of the extent of adsorption, effective completion being attained in 0.5 hour or less.

Adsorption is not easily reversed, severe treatment of the glass being necessary to remove the colloidal material.

The glass becomes "saturated" at a concentration of plutonium on the surface of about 1 $\mu g/cm^2$.

The practical applications of these facts to the analytical problem are immediately apparent. Serious loss of plutonium due to adsorption on glass surfaces is eliminated either by maintaining conditions under which the colloidal form of Pu(IV) is not produced (i.e., high acidity), or by working at such concentrations of plutonium that the area of glass exposed to the solution can have adsorbed at saturation less than the allowable error of the analysis. Material which has been adsorbed can be removed for analytical purposes by washing the surface with 3 M HF, concentrated H_2SO_4 (or sulfuric acid - dichromate cleaning solution) being preferred for mere purposes of decontamination.

III. NATURE OF THE ADSORPTION PROCESS

A. Experimental Work and Discussion: Since under optimum conditions only about half of the colloidal material was found to have been adsorbed, some characteristic of the reaction or of the reacting species must be interfering with the process. Already it has been seen that this is not a case of equilibrium in a rapidly reversible reaction: if it were, leaching of the glass would have been easily accomplished with a dilute acid wash.

The following experiment provides further evidence against such a picture. About 2 μg of plutonium as a colloidal sol was added to 0.5 ml of 0.1 M HNO_3 in a 1 ml Pyrex centrifuge cone. This solution was stirred mechanically for 12 hours at room temperature, after which time the liquid was transferred without washes to a second cone. The cycle was repeated several times, each time transferring to a clean cone; finally the solution was mounted directly on a platinum dish for counting. The adsorbed plutonium was then leached from the cone walls by two washes of 3 M HF, the washes from each cone being mounted on a Pt dish.

In this way the total amount of Pu(IV) present in each cone, and the fraction of this which was adsorbed in each case, were determined. The results of this experiment, performed in triplicate, are given in Table V.

As much as 1% in the columns labelled "% of Pu Adsorbed" (Table V) can easily be accounted for as held-up in the transfer

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TABLE V

Adsorption of Colloidal Pu(IV) by Glass

(Falling-off of Adsorption upon
Repeatedly Exposing the Solution to a Fresh Glass Surface)

(1)

Cone No.	Time of Contact	% of Pu Adsorbed
1	12 hrs.	56.5
2	"	4.95
3	"	1.20
4	"	0.84
5	"	1.13

(2)

Cone No.	Time of Contact	% of Pu Adsorbed
1	12 hrs.	50.2
2	"	2.63
3	"	1.39
4	"	0.42
5	"	0.57

(3)

Cone No.	Time of Contact	% of Pu Adsorbed
1	24 hrs.	49.5
2	"	3.35

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of liquid from cone to cone, due to the fact that no washes were employed. This means that essentially no adsorption occurred after contact with the second fresh glass surface.

If, then, cessation of the process is not due to establishment of equilibrium, why is it that only part of the colloidal material initially present can be adsorbed? Possible reasons are:

(1) Partial oxidation to the +6 state or reduction to the +3 state;

(2) Re-conversion to "normal" Pu(IV);

(3) Adsorption only of particles within a certain size limit, larger particles not adhering;

(4) Some change in the nature of the colloidal material, brought about by contact with the glass surface; this reaction, resulting in some form of Pu which could not be adsorbed, would compete with the adsorption process in using up the adsorbable material.

The answer to this question was to be found in absorption spectrum measurements. In order that these might be directly useful, the plutonium concentration should be approximately the same as in the sols from which adsorption had already been observed and measured, namely between 10^{-5} and 10^{-4} f. However, the low light absorption of such dilute sols presented a serious drawback: the Beckman spectrophotometer does not permit the use of cells which are long enough to give accurate log I_o/I readings. Use was therefore made of a laboratory-built spectrophotometer (v) which permitted a cell length of 50 cm, the volume of the cell

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used being 110 cm^3.

The colloidal sol used in this experiment was about 6×10^{-5} f in Pu(IV). One gram of Pyrex glass wool was employed for adsorption; this weight of glass wool was calculated to have a surface of about 2000 cm^2, an area slightly larger than that which could be "saturated" by this amount of plutonium. Thus conditions here were approximately the same as those prevailing in most of the adsorption experiments described in earlier sections, but on a much larger scale.

The sol was left in contact with the glass wool, with occasional stirring, for 3.5 hours. (Subsequent analysis showed that about 50% of the plutonium had been adsorbed.) The liquid was then poured into the 50 cm absorption cell and the spectrum was recorded. Since the base-line was not defined on this instrument, that shown in the figure (Fig. XXI) is arbitrary and for a rough reference only.

As the Beckman spectrophotometer offered distinct advantages in operating convenience and interpretation of results, it was decided to repeat the above experiment at high enough concentration of plutonium to permit use of the 10 cm cells in this instrument.

Here no attempt was made to adsorb out all of the colloidal material which was capable of adsorption. It was calculated that the amount of glass wool employed (again, approximately 1 gram) should have been saturated upon adsorbing about 25% of the total colloidal Pu(IV) present. Actually about 20% of the plutonium was adsorbed. The sol used was initially

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$4.5 \cdot 10^{-4}$ f in Pu; after 10 hours contact with the glass wool, the final concentration was $3.6 \cdot 10^{-4}$ f. Acidity (HCl) was 0.15 M.

The absorption spectrum was measured both before and after contact with the glass, a 0.15 M HCl solution being used as a blank. In Fig. IV are plotted the corresponding molal extinction coefficients vs. wavelength.

First of all, it is to be noted that the shape of the curve taken after adsorption is much the same in Fig. IV as in Fig. III. The important assumption is therefore made that the more concentrated sol has undergone the same change as has the more dilute sol. Thus conclusions drawn from the following observations, made with regard to the former (Fig. IV), may be applied equally to the latter and consequently to all the sols which have been investigated from the standpoint of adsorption alone.

Curve "a", Fig. IV, is typical of colloidal Pu(IV) sols (cf. Fig. I). Points of interest are:

(1) The absorption band of Pu(VI) at 8315 Å, indicating that about 20% of the material present was in this oxidized state;

(2) Bands at 7350 Å, 6200 Å, and 5800 Å, and the steep rise in absorption beginning at about 5300 Å, all characteristic of colloidal Pu(IV);

(3) The virtual absence of peaks indicating Pu(III) or "normal" Pu(IV).

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Curve "b" shows the following characteristics:

(1) Very high general absorption, rising in a fairly smooth curve of increasing steepness from the longest wavelength to the shortest;

(2) Presence of the same amount of Pu(VI) as before adsorption (now about 25% of the total plutonium present, since only the +4 state was removed)

(3) Peaks characteristic of colloidal Pu(IV) at 7350 Å and 6200 Å;

(4) Appearance of a small amount of "normal" Pu(IV), as indicated by a low peak at 4700 Å which did not occur in curve "a".

(For a detailed comparison of the absorption spectra of Pu, the reader is again referred to the following sources: (k),(l).)

These data are supplemented by an important observation made on the sol itself. After standing in contact with the glass wool the liquid became quite cloudy; in fact many particles were visible as such, and were easily precipitated by centrifugation. The observation was reproduced upon repeating the experiment.

This visible increase in particle size is correlated with the greatly increased light absorption throughout the wavelength region investigated. Curve "b" corresponds crudely to the $\frac{1}{\lambda^4}$-dependence of Rayleigh's scattering law, although no estimate of particle size is feasible on this basis.

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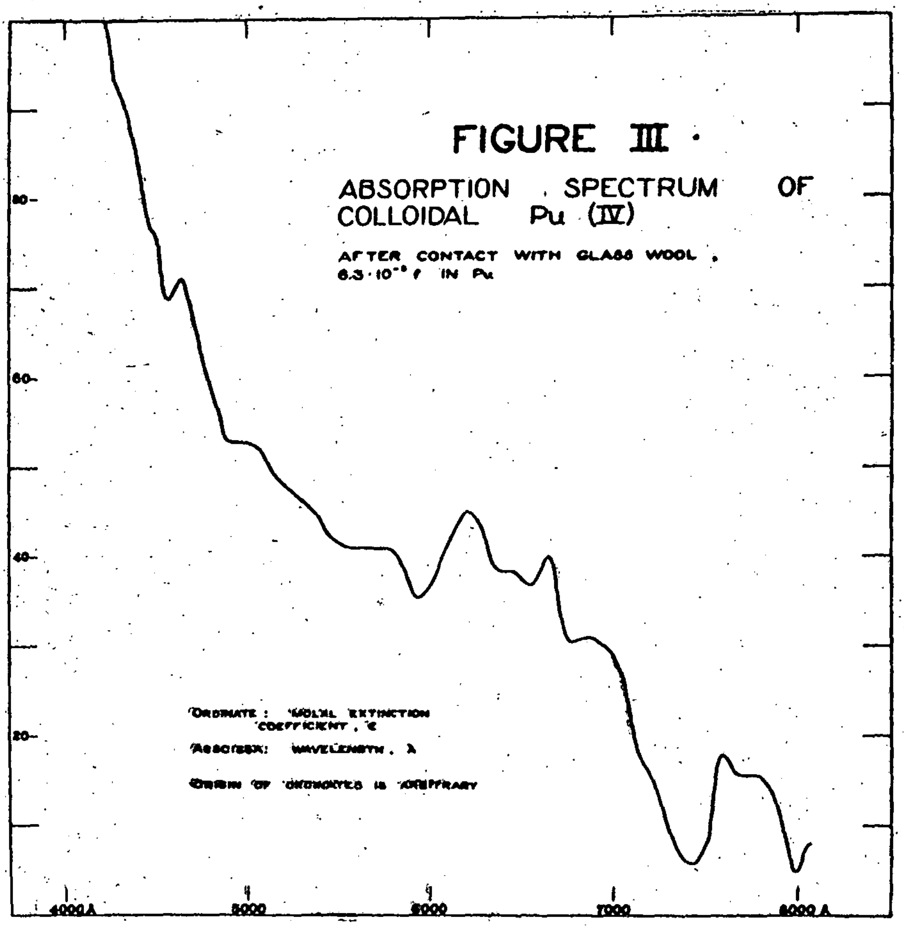

FIGURE III·

ABSORPTION SPECTRUM OF COLLOIDAL Pu (IV)

AFTER CONTACT WITH GLASS WOOL, $6.3 \cdot 10^{-5}$ f IN Pu

ORDINATE: MOLAL EXTINCTION COEFFICIENT, ε

ABSCISSA: WAVELENGTH, λ

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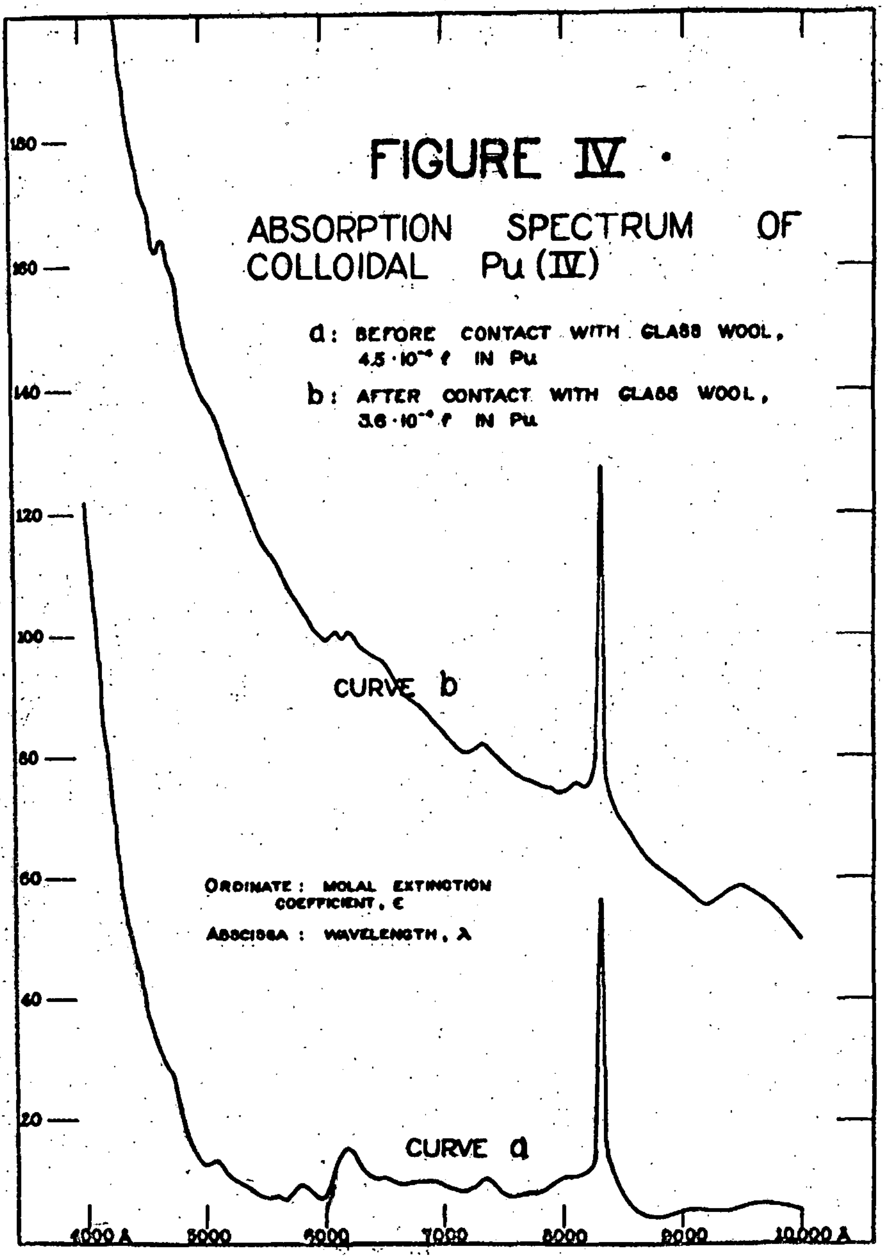

FIGURE IV ·

ABSORPTION SPECTRUM OF COLLOIDAL Pu(IV)

a: BEFORE CONTACT WITH GLASS WOOL, $4.5 \cdot 10^{-4}$ f IN Pu

b: AFTER CONTACT WITH GLASS WOOL, $3.6 \cdot 10^{-4}$ f IN Pu

ORDINATE: MOLAL EXTINCTION COEFFICIENT, ε

ABSCISSA: WAVELENGTH, λ

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It is apparent that no appreciable increase in Pu(III) or Pu(VI) had occurred. The amount of "normal" Pu(IV) ion had risen to only about 7% of the total plutonium present. Thus it is certain that adsorption does not cease due to oxidation or reduction or conversion to the "normal" +4 state; it seems, rather, that extensive growth of particles occurs under the influence of the glass, and that this causes the termination of the adsorption process.

The following experiment was then designed to compare qualitatively the extent of adsorption with particle size. A colloidal Pu(IV) sol 400 μl in volume, 0.002 f in plutonium and 0.1 M in HNO_3, was prepared for this work. A 100 μl portion was kept as control, while the remaining 300 μl was divided into two equal parts, these being placed in micro centrifuge cones. Centrifugation was carried out by means of a commerical high-speed air centrifuge, an acceleration of the order of 10^4 G's being maintained for about 4 hours; in this way a suitable segregation of particles according to size was effected.

At the end of this time the centrifuged samples were divided into three equal layers, corresponding portions from the two cones being combined. In addition an appreciable amount of sediment was observed on the bottoms of the cones. While this was not subjected to investigation, it will be considered in the discussion of the data obtained from this experiment.

The extent of adsorption was measured in exactly the same way for each sample, all experiments being run in duplicate. An aliquot containing about 3.5 μg of Pu was delivered into a 1. ml

Pyrex centrifuge cone containing 0.5 ml of 0.1 M HNO_3. This was allowed to stand with occasional stirring for 6 hours, after which time solution and glass were analysed separately for plutonium.

Absorption spectrum measurements were made on all solutions, namely the top, middle, and bottom layers of the centrifuged sol and the sample kept as control. From these the fraction of each sample which was in the colloidal state was estimated. (Due to the low light absorption of the less concentrated upper and middle layers, only safe limits are warranted from their spectra; the values given for the control and for the bottom centrifuged layer are probably accurate within a few per cent.)

Based upon the fraction of the total plutonium which was adsorbed, and the fraction which existed as colloidal Pu(IV), the extent of adsorption of the colloidal material alone was calculated. These data are summarized in Table VI below.

Assuming that in the entire centrifuged sample the concentration of plutonium, the fraction in the colloidal +4 state, and the fraction adsorbed were the same as in the control, these quantities can be calculated for the sediment which remained in the centrifuge cones. This has been done: these calculated values are also shown in the table.

Thus the correlation between glass adsorption and particle size is positively established, that the smallest particles of colloidal Pu(IV) are very highly adsorbed and that somewhere between the smallest and the largest particles existing in colloidal plutonium(IV) sols there is a size above which

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TABLE VI

Adsorption as a Function of Particle Size

(Centrifugation Experiment)

Sample and Volume	Conc. of Pu	% of Total Pu in Entire Centrifuged Sample	% of Pu found Adsorbed (2 Experiments)	% of Pu in the Colloidal +4 State	% of Colloidal Pu(IV) Adsorbed
Control, 100 µl	$1.32 \cdot 10^{-5}$f	—	34, 33	90	40
Top Centrifuged Layer, 100 µl	$2.8 \cdot 10^{-4}$f	5	33, 36	≤50 (42)	65-100 (80)
Middle Cont. Layer, 100 µl	$4.2 \cdot 10^{-4}$f	8	20, 36	≤70 (52)	50-80 (65)
Bottom Cont. Layer, 100 µl	$3.57 \cdot 10^{-3}$f	65	44, 42	93	50
Sediment [3]	—	22	7	100	7

[3] Entries opposite "Sediment" are calculated from the other data given in this table.

Where only crude limits are justified, the accompanying values in parentheses have been adopted for use in making the above calculations.

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virtually no adsorption takes place.

B. Conclusions — Probable Mechanism of the Adsorption of Colloidal Pu(IV) by Glass: The following is proposed as the most likely picture of the adsorption process. In some respects it is not sufficiently confirmed, and further investigations along these lines may be indicated; however, presentation of this scheme seems justified even though such additional evidence may be lacking.

(1) First, it has been demonstrated that the hydrous oxide, hydroxide, or basic salt which is known as colloidal Pu(IV) is a positive colloid (w). In this respect it does not stand alone: most metallic oxide colloids are known to be positively charged in acid.

(2) Second, it is known that such materials as paper, cotton, sand, and glass take on a negative charge when in the presence of water (x).

(3) It is not at all surprising that a positive colloid should adhere to a negatively charged surface. Negative adsorbents are utilized for the adsorption of positive particles, and vice versa (y). Similarly, in the realm of protective colloids it is known that positively charged colloidal particles will adhere to particles of opposite charge.(z)

(4) It might be expected that only small particles should be adsorbed, the larger ones not adhering for the simple reason that they cannot fit into the irregularities of the surface to permit close approach of charges.

(5) A clear picture of the aggregation process is more difficult to draw. However, other examples of the same type of phenomenon can be given. In the mutual precipitation of colloids by mixing a positive sol with a negative one, neutralization of charges results in the flocculation of both colloids. Weiser (x) states that positive colloids have been observed to lose their charge (and even in some cases to become negatively charged!) upon contact with such negative surfaces.

In view of this fact, it is safe to assume that aggregation due to loss of the stabilizing charge occurs under the direct influence of the negatively charged glass, although it is not clear why adsorption is not preferred to mere neutralization of charge when there is an excess of glass surface available.

Thus the adsorption of colloidal Pu(IV) may be looked upon as primarily an electrostatic phenomenon. Its irreversibility is probably due to the firmness with which the particles fit into the surface structure of the glass. The important factors in its occurrence are the area of glass available and a limiting particle size, the process terminating upon saturation of the glass or upon exhaustion of the supply of smaller particles by a combination of the adsorption process itself and the competing process of aggregation.

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References

(a) Kraus, CH-1764, p. 6.
(b) Werner and Moore, M-CH-1344, p. 8.
(c) Werner, M-CN-1254, p. 5.
(d) Cunningham, MUC-GTS-858, p. 1.
(e) Mc Lane, CH-1949, p. 4.
(f) Cunningham, CH-1368, p. 19.
(g) Werner, M-CH-2034, p. 5.
(h) Schubert, Conn, and Leslie, M-CH-2134, p. 15.
(i) King, CH-1134, p. 43.
(j) King, CN-1583, p. 15.
(k) Sheline, Kasha, et al, CH-1945.
(l) Sheline and Kasha, CH-[illegible], p. 64.
(m) Kraus, CH-1940, p. 10.
(n) Kraus, CH-2283, p. 17.
(o) Ref. (l), p. 47.
(p) Ref. (a), p. 16.
(q) Kraus and Hindman, CH-1048, p. 27.
(r) Ref. (n), Appendix.
(s) Clifford, Johnson, et al, CH-2040.
(t) Mc Lane and Dixon, CH-2030, p. 1.
(u) Ross, CH-2168, p. 2.
(v) Lewis, Lipkin, and Magel, J. Amer. Chem. Soc. 64, 3005
    (1941).
(w) The author, unpublished work.
(x) Weiser, INORGANIC COLLOID CHEMISTRY, John Wiley and
    Sons, Inc., vol. II, p. 52 (1935).
(y) Hauser, COLLOIDAL PHENOMENA, Mc Graw-Hill, Inc., 1st Ed.,
    p. 134 (1939).
(z) Ref. (y), p. 152.