653. *The Preparation and Properties of Some Plutonium Compounds. Part V.* Colloidal Quadrivalent Plutonium.*

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Colloidal, or polymeric, quadrivalent plutonium has been separated from the ionic species of plutonium by ion exchange. The absorption spectrum of the colloid is distinctive, quite different from those of other species of plutonium, and varies slightly with the method of preparation. The rate of formation of the polymer in dilute nitric acid, its stability in more concentrated acid, its adsorption on certain surfaces, and other properties have been studied. The minimum and maximum molecular weights of the colloid have been calculated from diffusion experiments and from work with nuclear emulsion plates.

THE existence of a colloidal, polymeric, form of quadrivalent plutonium has been known for many years. Most of the early work was done in America by Kraus, Werner, and others from 1944 to 1946 but, apart from general statements and a few diagrams,[1] few papers have been published. Thus it was known that the polymer, recognised by its bright green colour and diffuse absorption spectrum, was formed in quadrivalent plutonium solutions where the acidity was 0·2N or less. It could also be formed by heating solutions of low acidity. Kraus and Nelson [2] mention the colloid in general terms, comparing it with similar colloids formed by quadrivalent zirconium, uranium, and cerium. Work was also done at Harwell in 1950 by Hurst, Hall, Herniman, and Walter. The formation of the colloid and its absorption spectrum were studied but the results were not published.

In 1954 the production and some properties of colloidal plutonium(IV) in somewhat greater detail were described.[3] The characteristic maxima of the detailed absorption spectrum were given, together with a description of its absorptive properties, and various estimates of the molecular weight of the colloid particles. However, it was decided to investigate the preparation and properties of the colloid more thoroughly and if possible isolate the pure material by dialysis. The weak positive charge [3] of the colloid suggested ion exchange as another possible means of separation.

Solutions of colloidal plutonium(IV), also containing the ionic ter-, quadri-, and sexavalent states, were prepared by dilution of acid quadrivalent plutonium solutions with

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* Part IV, *J.*, 1956, 2565.

[1] "The Transuranium Elements," National Nuclear Energy Series, McGraw-Hill Book Co. Inc., New York, 1949, Vol. IV—14B, pp. 212, 215, 504, 572, 588.

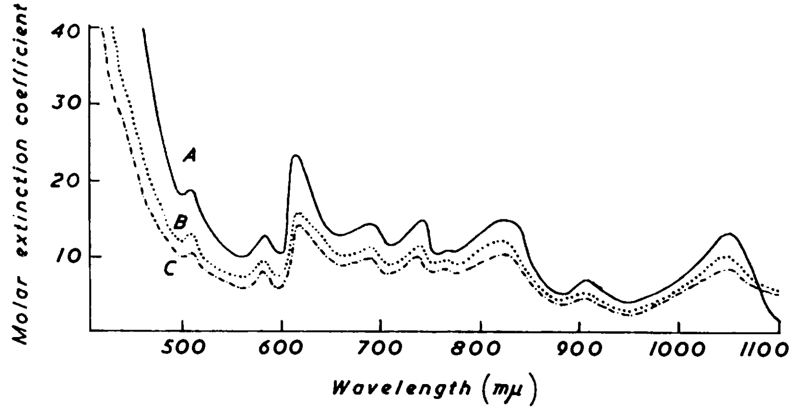
[2] Kraus and Nelson, U.S.A.E.C., Declassified Document, A.E.C.D. 1888.

[3] "The Actinide Elements," National Nuclear Energy Series, McGraw-Hill Book Co. Inc., New York, 1954, Vol. IV—14A, p. 317.

water. Similar solutions, containing plutonium(IV) colloid which had aged for about six months, were also available.

Dialyses with either parchment or Cellophane membranes were only partly successful, and since the procedure was tedious it was abandoned in favour of ion-exchange. Use of Amberlite IR-120 in the hydrogen form provided solutions of colloidal plutonium(IV) free from other plutonium species, and this method of separation was used from then on. Attempts to determine the distribution ratio of the colloid by equilibration gave impossibly high values, probably owing to adsorption on the resin instead of exchange. Three solutions of pure colloidal plutonium(IV) were obtained by the ion-exchange method: a solution of aged colloid, a solution freshly prepared by dilution with water, and another prepared by dilution with 0·1M aqueous ammonia.

FIG. 1. *Absorption spectra.*



A, Aged colloidal Pu^{IV} prepared by dilution with water; *B*, Fresh colloidal Pu^{IV} prepared by dilution with water; *C*, Fresh colloidal Pu^{IV} prepared by dilution with aqueous ammonia.

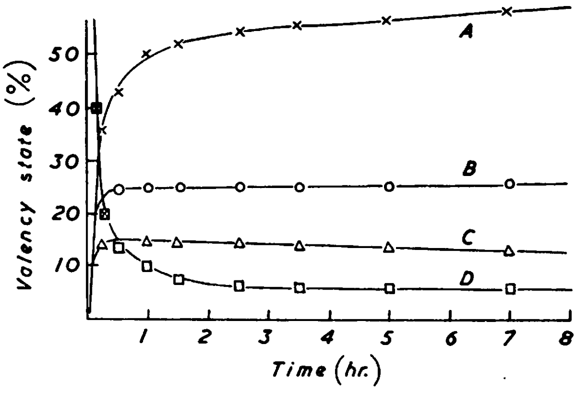


FIG. 2. *Equilibration of valency states of plutonium.*

A, Colloidal Pu^{IV}; *B*, Pu^{III}; *C*, Pu^{VI}; *D*, Pu^{IV}.

The absorption spectra of these solutions are shown in Fig. 1. They are quite distinct from each other, but their shapes are the same, with corresponding absorption peaks at the same wavelengths. The method of preparation, and the age of the colloid, obviously affect the spectrum considerably. The American workers almost certainly isolated the pure material, probably by dialysis although no method was described, since the spectra found by them ($\lambda_{max.}$ 510, 579, 618, 817 mμ; Kraus [3]) are almost identical with ours ($\lambda_{max.}$ 510, 580, 615, 690, 740, 825, 910, and 1045 mμ).

Having established the complete absorption spectrum of fresh colloidal plutonium(IV) it became possible to measure its approximate rate of formation in a diluted quadrivalent plutonium solution. The spectra of all the ionic valency states of plutonium being well established, the proportions of each were easily calculated. The results (Fig. 2) show that the colloid is formed extremely quickly in 0·1M-nitric acid, over 40% being formed in the first thirty minutes. Disproportionation $3Pu^{IV} \rightleftharpoons 2Pu^{III} + Pu^{VI}$ competes,[4] and after several hours the solution reaches an almost steady state with about 55% of colloidal quadrivalent plutonium, 25% of the tervalent state, and smaller amounts of the other valency states. Thereafter the proportion of colloidal plutonium(IV) increases very slowly to a maximum of about 75%.

It is well known that quadrivalent plutonium forms strong complexes with the nitrate ion,[5] a situation which would always tend to oppose formation of the colloid. In 0·1M-nitrate ion solutions the colloid is formed immediately and it was therefore decided to investigate its formation in solutions of low acidity and high nitrate concentration. Solutions of concentrated quadrivalent plutonium nitrate diluted with ammonium nitrate solutions of increasing concentration were examined spectrophotometrically. The solutions were initially brown, owing to the $PuNO_3^{3+}$ ion,[5] but most became bright green, quickly or slowly according to the concentration of ammonium nitrate used. Below 0·5M-nitrate ion the colloid formed very quickly, between 1 and 2M it formed slowly, finally being precipitated as a green solid, while only in nitrate solutions above 4M was its formation prevented.

The rates of conversion of the colloid into ionic quadrivalent plutonium, by the action of nitric acid of varying concentrations, were then studied spectrophotometrically. The results (Table) show clearly the difference between the fresh and the aged form of the colloid, the former being converted by the nitric acid in a matter of days at room temperature, the latter being precipitated at low acid concentrations. The difference in behaviour of the two forms possibly lies in the increased size and smaller charge of the colloidal particles in the aged form. These results agree with the general statements published by the American workers, who found that the colloid was slowly converted into the ionic form by 1M-nitric acid and showed that many electrolytes would precipitate the colloid.[3] Examination of the colloid, precipitated as described above, by *X*-ray diffraction showed it to be very similar to freshly precipitated quadrivalent plutonium hydroxide. Both the *X*-ray patterns were extremely diffuse, showing a faint plutonium dioxide structure, suggesting that the precipitated colloid and quadrivalent plutonium " hydroxide " are just hydrated plutonium dioxides.

TABLE. *Rate of conversion of the colloid into ionic form (hr.)*

HNO_3 (M)	1	3	5			
Temp.	—	—	18°	50°	70°	90°
Fresh colloid	120	90	24	—	—	—
Aged colloid	Precipitated	Precipitated	>200	10	4	2·5

It was expected that in common with other colloids the polymeric form of plutonium(IV) would be adsorbed on surfaces with which it came into contact. This had been indicated by Carniglia [3] and was confirmed in these laboratories. Our value of 1·6 µg. cm.$^{-2}$ for glass agrees well with Carniglia's figure [3] of 1 µg. cm.$^{-2}$, though this is probably coincidental since the adsorption will depend largely on the type of surface involved. On steel, for example, the adsorption was found to be much higher.

It was thought that the colloid might behave optically like a true ionic solution and this was demonstrated (Fig. 3) by application of Beer's law and Lambert's law to both the fresh and the aged form. The two laws are obeyed by the colloid, in both its forms, but unfortunately this fact is of little use for accurate determination of the colloid since each solution would have different molar extinction coefficients at the wavelengths used.

The behaviour of the colloid towards solvent-extraction was examined by using solvents and conditions under which quadrivalent plutonium is extracted. Use of dibutylcarbitol (diethylene glycol dibutyl ether), trifluorothiophenoylacetone in benzene, and tributyl phosphate in kerosene under the appropriate conditions showed that extraction of the colloid, as expected, was negligible. In the case of tributyl phosphate, however, one

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[4] Ref. 1, p. 295.

[5] Ref. 1, p. 388.

Plate 1. Colloidal plutonium(IV). (×187.)

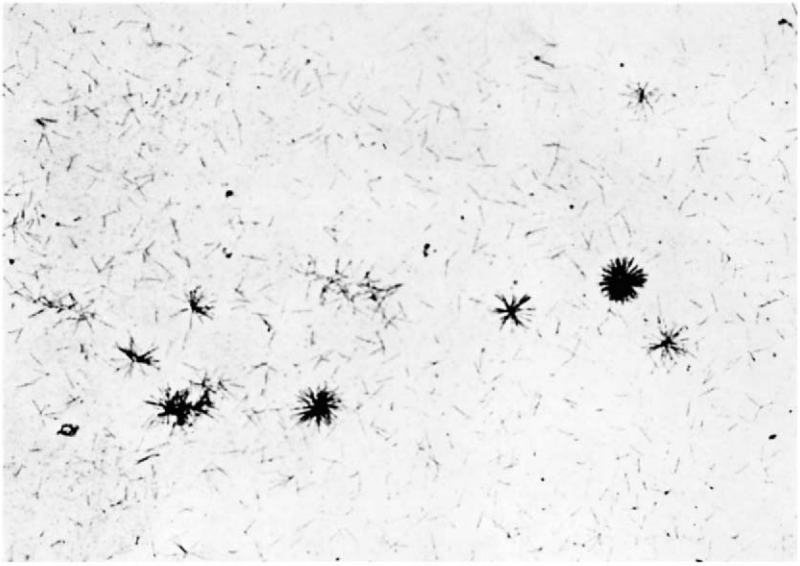
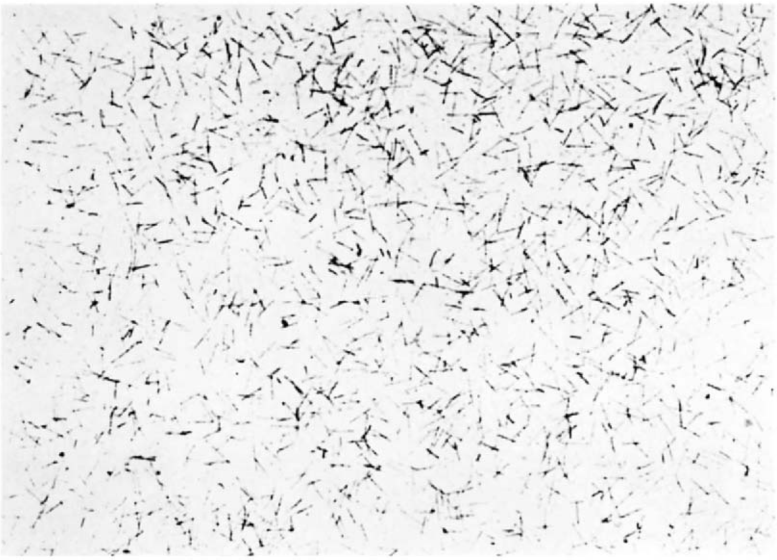


Plate 2. Ionic plutonium(III). (×187.)

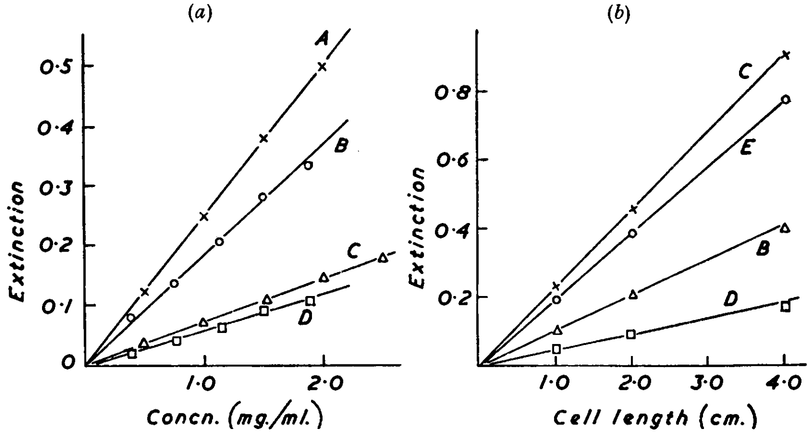


[*To face p.* 3360.

experiment gave a partition coefficient of 35, due entirely to traces of dibutyl phosphate in the solvent. Further extraction experiments on the colloid in dilute acid with 5% dibutyl phosphate in kerosene gave high partition coefficients, the colloid entering the organic phase unchanged, as shown spectrophotometrically. It was also possible to extract colloidal ferric hydroxide into the same solvent with chloroform as a diluant. The mechanism of these extractions is not clear. In all experiments there was slight precipitation at the solvent–aqueous interface, the effect becoming very marked with aged colloid solutions.

High-speed centrifuge experiments (7000 *g*) on solutions of aged polymer indicated that the molecular weight was extremely high, since most of the colloid could be centrifuged from solution in a few hours. A similar result was obtained with solutions of colloidal ferric hydroxide. The effect on solutions of fresh colloidal plutonium(IV) was very much less, only a very small fraction being centrifuged in the same time. Work with Ilford nuclear emulsion plates showed that the molecular weight of both forms was indeed very high. The colloid, obviously composed of particles of very different sizes, showed itself as characteristic "stars," each of which had been made by the α-particle tracks from a single colloid particle (Plate 1). On the other hand, plates treated with ionic plutonium showed a completely random distribution of α-particle tracks (Plate 2). Calculations made from the number of tracks in the larger "stars" showed that the maximum molecular weight was of the order of 10^{10}. The fact that both the fresh and the aged form of colloidal plutonium(IV) gave similar results by the nuclear plate technique was unexpected. Possibly the aged form contains a much greater number of medium-sized particles which, although capable of being centrifuged, would not be detected by the nuclear plate technique.

FIG. 3. *Conformance with* (*a*) *Beer's law and* (*b*) *Lambert's law.*



A, Aged colloid (440 mμ).
B, Fresh colloid (440 mμ).
C, Aged colloid (615 mμ).

D, Fresh colloid (615 mμ).
E, Aged colloid (510 mμ).

The minimum molecular weight of the colloid was estimated by diffusion in an apparatus similar to that used by Anderson and Saddington.[6] The diffusion of fresh dilute colloid solutions was followed, ^{238}Pu being used as tracer. Comparison of this diffusion with that of a known ionic species,[4] $Pu(NO_3)_6^{2-}$, by use of the Graham–Riecke relation [6] showed that the minimum molecular weight was about 4000. These results show that the molecular weight of colloidal quadrivalent plutonium lies between extremes, and both the maximum (10^{10}) and minimum (4×10^3) figures are therefore only approximate. These values are well outside those quoted by American workers, who found values of $4{\cdot}2 \times 10^5$ by diffusion and 2×10^7 by ultracentrifugation. The method of preparation is possibly a factor in these differences.

[6] Anderson and Saddington, *J.*, 1949, S381.

EXPERIMENTAL

Apparatus.—Spectrophotometric measurements were made with a Hilger "Uvispek" spectrophotometer, 1 cm. glass cells being used except where stated. Water was used as the control.

Preparation and Purification of Colloidal Solutions.—All solutions were prepared by dilution with water of quadrivalent plutonium nitrate in nitric acid. This procedure gave solutions of the correct acidity (0·1M) at concentrations (1—3 mg./ml.) suitable for spectrophotometric analysis. The aged solutions were kept for a long period before purification.

The slow passage of a solution (10 ml.) down a 1 ml. burette packed with Amberlite IR-120 resin in the hydrogen form provided a solution of quadrivalent plutonium colloid which showed no detectable trace of other valency states. The concentration of each solution so prepared was found by α-particle counting. Solutions prepared in this way showed no change in concentration after further ion exchange.

Conversion of the Colloid into the Ionic Form.—A solution of colloidal plutonium(IV) (5 ml.) was diluted with nitric acid (9M) to give a solution of the required acidity. The spectral changes of the solution were then followed in a spectrophotometer.

X-*Ray Examination of Precipitated Colloidal Plutonium.*—Nitric acid (9M; 1·2 ml.) was added to a solution of the aged colloid (10 ml.) and the mixture well stirred. After 5 min. the light-green solid which had separated was collected, washed several times with very dilute nitric acid and finally with a little water and dried with acetone. The solid was then submitted to *X*-ray analysis. A similar procedure was followed for freshly precipitated quadrivalent plutonium hydroxide, prepared by addition of ammonia solution to plutonium nitrate solution.

Adsorption Experiments.—A thin microscope slide, a steel counting tray, and a piece of sheet steel were immersed in fresh colloidal plutonium(IV) solution for 7 days. They were then removed and washed well with 0·1M-nitric acid and the activity was removed from each sample by hot 5M-nitric acid. The solutions obtained were then analysed for plutonium by α-counting. The results are shown below :

	Total area (cm.^{2})	Total activity (μg.)	Absorption per cm.^{2} (μg.)
Glass slide	12·5	20·1	1·6
Steel tray (polished)	11·0	45·0	4
Sheet steel (unpolished)	6·7	70·5	11

Conformance with Beer's Law.—Solutions were prepared containing from 1 to 5 ml. of colloidal plutonium(IV) solution (2·4 g./l.) and 0 to 4 ml. of 0·1M-nitric acid. The extinction of solution was measured at 440 and 615 mμ for both fresh and aged colloid. By using 1-, 2-, and 4-cm. cells it was shown that the polymer in both forms also obeyed Lambert's law.

Solvent-extraction Experiments.—Fresh colloidal plutonium(IV) solution was adjusted to the required acidity and the solvent equilibrated with an aqueous solution of the same acid strength. 1 ml. portions of each solution were shaken together in a stoppered tube for 10 min. The plutonium content of each layer was then determined by α-counting.

Solvent	Average Pu in solvent (μg.)	Average Pu in aqueous layer (μg.)	*K*
Diethylene glycol dibutyl ether	11·7	200	6×10^{-2}
0·2M-Trifluorothiophenoylacetone–benzene	7·7	1530	5×10^{-3}
20% Tributyl phosphate–kerosene	96	600	0·16
5% Dibutyl phosphate–kerosene	990	25	40

Estimation of Molecular Weight.—(a) *Centrifugation experiments.* Portions (3 ml.) of an aged colloid solution in a series of 5 ml. centrifuge tubes were centrifuged at 7000 ***g*** in a high-speed centrifuge for increasing periods. At the end of each period a tube was removed, the supernatant liquid removed, and the precipitated solid dissolved in nitric acid (8M). The plutonium content of this solution was then found by ordinary counting techniques. Both forms of the colloid were examined in this way, periods up to 5 hr. being used.

	Colloid centrifuged at 7000 ***g*** (%)				
Time (min.)	10	45	90	180	300
Aged colloid	7	30	55	75	85
Fresh colloid	—	—	—	—	5

(b) *Nuclear emulsion plate experiments.* Dilute solutions (10^{-7}M) were prepared of both the fresh and the aged colloid in 0·1M-nitric acid, as well as an ionic (tervalent) form of plutonium in 0·1M-hydrochloric acid. The nuclear emulsion plates (Ilford Type C.2, 50 μ) were immersed in each solution for 10 min., washed with very dilute acid, dried, and stored in the dark for several days. They were then processed and examined in a projection microscope. Photographs (Plate 1) were taken of the stars and " clumps " formed by the colloid particles, together with the random α-tracks shown by ionic plutonium (Plate 2). After allowance for a geometry factor of 3 it was seen that an average large colloid particle had given about 60 α-particles in, say, 11 days. From the specific activity of plutonium ($1·4 \times 10^5$ disintegrations min.$^{-1}$ μg.$^{-1}$) and Avogadro's number the molecular weight was calculated to be about 10^{10}.

(c) *Diffusion experiments.* An apparatus similar to that used by Anderson and Saddington [6] was constructed, with capillaries 2 cm. in length and 1·5 mm. in internal diameter. Colloid solutions were used which contained about 1 μg. of plutonium/ml.; the solution placed in the capillaries contained 90-year ^{238}Pu, which, while giving an appreciable α-count, was in negligible concentration. The diffusion apparatus was kept for 20 days in an insulated box and the change in the ^{238}Pu : ^{239}Pu ratio (caused by the diffusion of the " tagged " colloid *out* of the capillaries and the diffusion *in* of normal colloid from the surrounding bulk solution) followed by means of an α-pulse amplitude analyser. A similar experiment was performed using plutonium solutions in 8M-nitric acid. The results are as follows :

Species	Time of diffusion (hr.)	^{239}Pu (%)	^{238}Pu (%)	γ
$Pu(NO_3)_6^{2-}$	0	25 ± 1	75 ± 2	0·05
	620	96 ± 4	4 ± 1	
Colloid	0	$17 \pm 0·7$	83 ± 2	0·98
	500	$19 \pm 0·7$	81 ± 2	

The diffusion coefficient, is given by

$$D = \frac{4l^2}{\pi^2 t} \ln \frac{8}{\pi^2 \gamma} \text{ (ref. 6)}$$

where l = length of capillary (cm.), t = time of diffusion (sec.), and γ = fraction of tracer left in capillary after time t.

By the Graham–Riecke relation, $D_1\sqrt{M_1} = D_2\sqrt{M_2}$, where D_1 and D_1 are diffusion coefficients and M_1 and M_2 are molecular weights. If D_1 and M_1 refer to the $Pu(NO_3)_6^{2-}$ ion ($M_1 = 612$) and D_2 and M_2 to colloidal plutonium, then

$$D_1/D_2 = \sqrt{M_2}/\sqrt{M_1} = (t_2 \log \gamma_2)/(t_1 \log \gamma_1)$$

Substitution of the appropriate values gives M_2 about 4000. This is obviously only the order of the minimum molecular weight.

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