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SOME FACTORS AFFECTING THE CUPFERRON EXTRACTION PROCEDURE FOR ESTIMATION OF TRACE AMOUNTS OF PLUTONIUM

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ABSTRACT

The effects of a number of factors on the cupferron extraction of plutonium have been observed during attempts to apply it to the analysis of biological materials. These effects are presented in some detail. The ferric cupferride complex is shown to be stronger than the plutonium cupferride complex. A method is proposed for the assaying of hexavalent plutonium for small amounts of reduced plutonium. The method is based on the cupferron extraction.

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SOME FACTORS AFFECTING THE CUPFERRON EXTRACTION PROCEDURE FOR ESTIMATION OF TRACE AMOUNTS OF PLUTONIUM

INTRODUCTION

Trace amounts of plutonium can be separated quantitatively from relatively large volumes of solutions by the cupferron extraction method. Considerable information regarding the cupferron extraction of plutonium has been collected during numerous attempts to adapt the procedure to the analysis of biological materials. It is believed that some of this information may be of general interest.

METHOD OF EXTRACTION

The cupferron method of extracting plutonium used in this laboratory, is briefly as follows:

The solution to be extracted is placed in a separatory funnel and the acidity adjusted with NH_4OH either to the green of methyl violet or, in the case of urine, feces, and bone ash solutions, to the point of precipitation of Ca and Mg salts where the concentration of these metals is high. At least 1 ml of 6% aqueous cupferron solution is added and the separatory funnel shaken for one-half minute. If the iron content is high, as shown by a voluminous red-brown precipitate, more than one ml of cupferron should be added. After shaking with the cupferron, 2 ml of $CHCl_3$ are added and the funnel again shaken for one-half minute. The $CHCl_3$ is drawn off, and a second portion of $CHCl_3$ added, shaken, and drawn off. This process is repeated until the $CHCl_3$ is colorless; 4 or 5 portions are usually sufficient. If the addition of a few drops of cupferron to the sample now produces a white precipitate, the extraction is complete. If a red-brown precipitate forms, iron is still present, and the extraction must be repeated.

The $CHCl_3$ phases are combined in a 40-ml centrifuge tube and evaporated to dryness in a water bath at 70° C. The residue is treated with about 1 ml

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conc. HNO_3 and allowed to remain in the water bath at 70° C for 15 to 20 minutes. At the end of this time, 1 ml 72% $HClO_4$ is added and the mixture placed in an oil bath at 130° C. The temperature is gradually raised to 180° C over a period of an hour. A pale-yellow solution results, which becomes colorless upon cooling.

The cool solution is diluted to 4 ml with water. Two drops of 20% $NH_2OH \cdot HCl$ are added and the solution allowed to stand one-half hour. Two hundred micrograms of La^{+3} are then added followed by 0.5 ml 27 N HF. The tube is centrifuged 15 minutes at 2000 RPM, the precipitate of LaF_3 is washed with 2 ml of 0.1N HF, slurried to a Pt foil, dried, flamed, and counted in an alpha counter. If the LaF_3 is not centrifuged immediately after the addition of HF, the glass may be attacked, leading to a large amount of precipitate which will cause trouble when the LaF_3 is transferred to the foil.

FACTORS AFFECTING CUPFERRON EXTRACTION OF PLUTONIUM

Extractable Forms of Plutonium

W.H. Langham (CK-1756) has studied the cupferron extraction of the various valence states of Pu on the milligram scale. The trivalent and the tetravalent ion extract equally well, whereas the hexavalent Pu is only partially removed, the amount depending on the effectiveness of reducing agents which may be present to convert the plutonium to an extractable reduced form. That the same holds true on a tracer scale (CK-738) has been confirmed in this laboratory. Hydroxylamine hydrochloride is used as a reducing agent prior to cupferron extraction in the above method if the presence of hexavalent plutonium is suspected.

Carrying Power of LaF_3 in the Cupferron Method

The LaF_3 assay technique for trace amounts of plutonium has been shown to

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be essentially quantitative in $HClO_4$ solutions up to 6 N and with amounts of La from 50 micrograms to 1 milligram in a volume of 4 ml. Conditions of the experiment were as follows:

Four ml of $HClO_4$ solution in a 40-ml centrifuge tube was spiked with 450 c/m of plutonium. Two drops of 20% NH_2OH-HCl were added and the solution allowed to stand one-half hour. Variable amounts of La^{+3} and 0.5 ml 27N HF were added, the tube centrifuged 15 minutes at 2000 RPM and the supernatant liquid decanted again. The precipitate was slurried onto a platinum plate with water, evaporated to dryness, flamed, and counted.

The results are presented in Table I.

TABLE I. Effect of $HClO_4$ Conc. and Amount of La^{+3} on the Carrying of Pu by LaF_3*

	Percent of Pu Carried With Variable Amounts of La^{+3}				
Conc. $HClO_4$	50 γ La^{+3}	100 γ La^{+3}	200 γ La^{+3}	500 γ La^{+3}	1000 γ La^{+3}
1 N			95%	95%	
2 N	93%	95%	95%	94%	94%
4 N			94%		
6 N			93%		

* Each value represents an average of at least four determinations, 4% maximum deviation from the mean.

It is evident that the acid concentration and the amount of lanthanum used are not critical factors in the assay of the wet-ashed $CHCl_3$ phase previously described.

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Effect of Phosphate Ion on the Efficiency of Extraction

The efficiency of the cupferron extraction of trace amounts of "reduced" plutonium from H_2SO_4 solution has been reported to drop markedly at a $pH < 0.8$ (CK-801). Also, it has been found in this laboratory that extraction of plutonium from 0.2M $HClO_4$ is less consistent and complete than from 0.2M HCl or HNO_3. Extraction from human feces and rat skeleton ash solutions (high in phosphate) also is inconsistent. When present in large amounts, anions which tend to complex Pu apparently prevent complete extraction with cupferron into $CHCl_3$.

A quantitative study of the effect of phosphate at three pH ranges has been made. The results are presented in Table II. Total phosphate content ranged from 0.005 gm to 1.0 gm, at pH values of 1, 2, and 4; the total volume was approximately 40 ml in all cases.

The curves obtained by plotting recovery versus phosphate concentration for each pH value are erratic and show only a general trend toward lower recoveries as the phosphate content increases. As the curves are erratic a correction factor cannot be applied to solutions whose phosphate content is known. For each phosphate content the recoveries are the same within experimental error at each pH. The highest recovery (at 0.005 gm $PO_4^{\equiv}$/40 ml) is about 90%. Each value in Table II was determined by at least two cupferron extractions.

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TABLE II. Effect of Phosphate on Extraction of Pu With Cupferron

Gm $PO_4^{\equiv}$ in 40 ml	Recovery in Percent			Average Recovery
	pH = 1	pH = 2	pH = 4	
0.005	91.2	87.4	89.2	89.3% ± 2.0%
0.01	84.9	83.0	84.5	84.1% ± 1.0%
0.03	89.4	88.4	88.0	88.6% ± 0.7%
0.05	88.2	77.6*	85.8	87.0% ± 1.2%
0.10	81.4	79.8	80.8	80.7% ± 0.8%
0.30	81.1	82.6	83.9	82.5% ± 1.4%
0.50	77.7	74.7	74.7	75.7% ± 2.0%
0.70	82.2	83.6	86.8	84.2% ± 2.5%
1.00‡	69.7	73.1	81.5	‡

* This result was omitted from averaged results.

‡ No average made as results are too erratic. At this concentration of $PO_4^{\equiv}$, it is very difficult to adjust the pH.

As phosphate interferes with the recovery of plutonium, a calcium oxalate carrying procedure for trivalent Pu, preliminary to a cupferron extraction, has been developed for the assay of human feces. Overall recovery by this method has been consistently better than 80%. Details of the method may be found in LA-376.

Effect of Acidity and Volume on the Extraction of Pu From HCl Solution

Studies have been made of the cupferron extraction of Pu from HCl solution containing no inorganic constituents and from a mock urine ash solution containing the following:

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10.0 gm NaCl
4.0 gm K_2SO_4
0.74 gm $CaCl_2 \cdot 2H_2O$
1.69 gm $MgCl_2 \cdot 6H_2O$
2.42 gm $NaH_2PO_4 \cdot H_2O$

} per 100 ml in dilute HCl

(100 ml contains the inorganic constituents of an average 24 hour specimen of human urine.)

Mock solutions to which known amounts of Pu had been added, were extracted, some containing no iron and some containing 24 mg $FeCl_3 \cdot 6H_2O$ (5 mg Fe^{+3}), to determine whether the presence of another extractable metal would affect the recovery of Pu. Iron is the only metal consistently present in biological materials which extracts by the cupferron method.

TABLE III. Effect of Acidity and Presence of Fe on Extraction of Pu With Cupferron*

Soln.	Vol.	0.2N HCl	0.5N HCl	1.0N HCl	1.5N HCl	2.0N HCl
HCl	25 ml	95%				
HCl	50 ml	93%				
HCl	100 ml	88%	87%			
mock sol. (with Fe)	100 ml	90%	90%	88%	80%	71%
mock sol. (no Fe)	100 ml	87%	85%	83%	73%	56%

* These results are not corrected for the expected loss of about 5% from the LaF_3 assay of the $CHCl_3$ phase.

All extractions were made using 1.5 ml of 6% cupferron solution and several 2 ml portions of $CHCl_3$ until the final portion of $CHCl_3$ was colorless. The $CHCl_3$ phase was wet-ashed and assayed according to the LaF_3 method described earlier in this report.

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The results presented in Table III show that the acid concentration does not seriously affect recovery in the range 0.2 to 1.0 N in HCl. Recovery in this range is consistent. The maximum deviation from the mean in a large series of determinations was 4%. However, it has been observed that the recovery of low counts (100 c/m and less) decreases somewhat more with increasing acid concentration and is more erratic than the recovery of larger amounts (1000 c/m). When the HCl concentration is above 1 N recovery is more erratic. The data presented in Table III are shown graphically in Fig. I.

Thus in the assay of any biological solution by the cupferron extraction method, the acidity is adjusted either to the green of methyl violet ($pH \sim 0.3$) or to the point of precipitation of the inorganic constituents.

Effect of Iron

Apparently the presence of a small amount of iron is beneficial to the extraction of Pu by cupferron (Fig. I). When using spikes of 5 c/m and 10 c/m, the effect of iron is more pronounced. From 100 ml of mock solution (neutralized to the point of precipitation) containing no iron, recovery of 10 c/m was extremely erratic, whereas from a similar solution containing 1 mg Fe^{+3}, recovery was consistently in the range 85 to 100% with an average recovery of 93% 1).

Thus, in the assay of human urine and feces samples, where low counts are expected, 1 mg of Fe^{+3} is added previous to the cupferron extraction 2). In the assay of animal tissue and excreta, no iron is added when the count is expected to be high.

The iron must be extracted completely in order to effect a complete extraction of plutonium. Two experiments were conducted to determine the relative strengths

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1) These values are corrected for the average blank determination of 0.5 c/m.

2) A more detailed report of low count recoveries from human urine will be found in LA-349.

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of the Fe and Pu cupferride complexes.

1) A Pu tracer solution (reduced with $NH_2OH \cdot HCl$) was shaken vigorously for one hour with a suspension of about 100 mg of ferric cupferride in 100 ml of 0.2N HCl (the iron complex had been carefully washed free of excess cupferron). The suspension was then extracted with $CHCl_3$ and assayed in the usual way. Two determinations gave results of 8% and 13% of the Pu in the $CHCl_3$ phases.

2) A 100-ml spiked mock urine ash solution (0.5N HCl) was treated with half the stoichiometric amount of cupferron necessary to react with the 4 mg of Fe^{+3} present. An extraction was performed in the usual way and 3% of the Pu was found in the $CHCl_3$.

These two experiments indicate that the cupferride complex of Fe is much stronger than that of Pu. Hence, all the iron must be extracted in an assay for Pu.

If a solution contains a large amount of iron, it is difficult to know when enough cupferron has been added. In such cases, a quantity of cupferron (2 to 3 ml) is added and the solution extracted with several portions of $CHCl_3$. More cupferron is then added. If a white precipitate forms, the extraction is complete. If a red-brown precipitate forms the extraction of Fe^{+3} is not complete and a second extraction must be performed. The combined $CHCl_3$ portions are assayed for Pu in the usual way.

Stability of Aqueous Cupferron Solutions

At room temperature, a 6% solution of cupferron gradually decomposes. The solution becomes highly colored, and decomposition products settle out. It has been found in this laboratory that solutions which have been standing for as much as five or six days often lead to low recovery of trace amounts of Pu. Therefore, it is recommended that a fresh solution be prepared at least every four days.

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A METHOD FOR ASSAYING HEXAVALENT PLUTONIUM FOR SMALL AMOUNTS OF REDUCED PLUTONIUM

Hexavalent Pu cannot be extracted into chloroform as a cupferron complex. However, cupferron itself will reduce part of the Pu to a valence state which is extractable. W.H. McVey, (CN-1588) suggests 0.05N $Cr_2O_7^{=}$ + 1N HNO_3 as a holding oxidant for hexavalent Pu in connection with a LaF_3 separation of the reduced Pu that may be present. Dichromate in acid solution attacks cupferron, so a cupferron extraction of reduced Pu from a basic solution in the presence of dichromate has been developed.

The hexavalent plutonium, in amounts up to 50,000 c/m, was made 0.05 N with respect to $Cr_2O_7^{=}$ and 1% with respect to sodium citrate in a total volume of 10 ml. The citrate prevents hydrolysis of the plutonium in basic solution. The solution was neutralized to the phenol red endpoint with NH_4OH and extracted with ten drops of 6% cupferron and four portions of $CHCl_3$. The $CHCl_3$ phase was wet-ashed and assayed by the LaF_3 technique as already described.

A large series of "blank" determinations were made to ascertain how much hexavalent plutonium carries through the extraction. A reproducible blank of 2.5% was found in a series of 15 determinations using 9,000 c/m of hexavalent Pu. A blank of 1.5% was found using 50,000 c/m of hexavalent Pu. This quantity, since it varies with the amount of Pu, probably is due to a mechanical contamination of the $CHCl_3$ rather than an actual partition of hexavalent Pu cupferride. If so, an extraction from a larger amount of hexavalent Pu might lower the blank and therefore offer a distinct advantage over the LaF_3 separation of valence states, in which a 3.8% "blank" is reported (CN-1588).

Recovery of reduced Pu (Pu^{+3} and Pu^{+4} extract equally well) by this method averaged 86% in a series of 12 determinations with a maximum deviation of 3%. The application of a 15% correction to the cupferron extraction procedure plus the LaF_3 assay is justified on the basis of a large number of determinations

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made in this laboratory. This would give an excellent recovery of reduced Pu from hexavalent Pu.

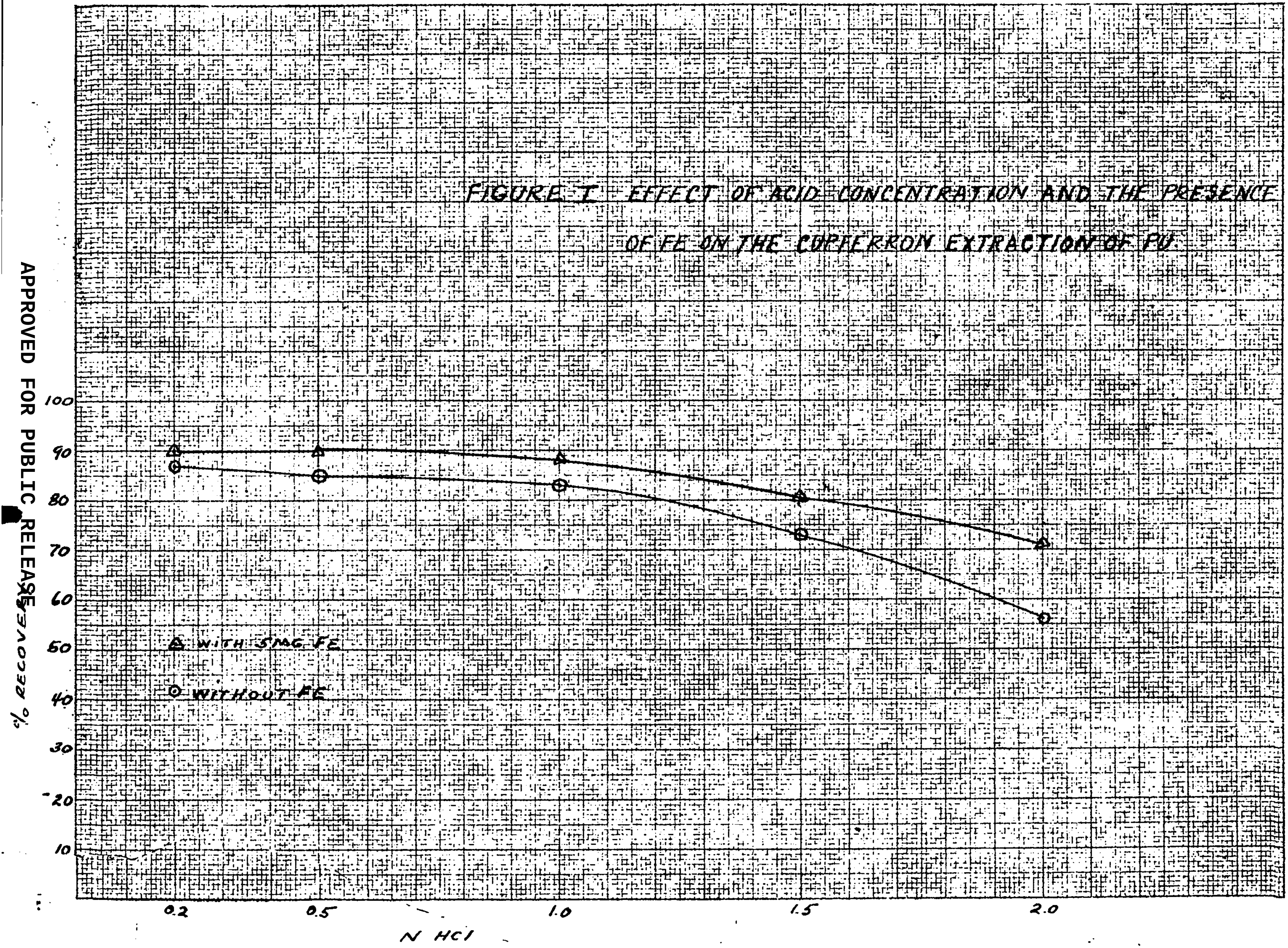

FIGURE I EFFECT OF ACID CONCENTRATION AND THE PRESENCE OF FE ON THE CUPFERRON EXTRACTION OF PU.

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