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✓ 4.2 Radiation chemistry

4.2.1 Radiation chemistry of plutonium in nitric acid solutions

P.R. Natarajan, M.S. Nagar and S.K. Gupta

a) Spectrophotometric analysis

The object of this work is to standardise a spectrophotometric method to determine the concentrations of Pu(III), Pu(IV) and Pu(VI) in nitric acid solutions with a view to applying the method for analysing gamma irradiated plutonium solutions. For this purpose pure Pu(III) solutions were prepared by adding excess of hydroxylamine hydrochloride to plutonium solutions. Because of the oxidising nature of nitric acid, Pu(III) solutions could be studied only up to 4M HNO₃. Pu(IV) solutions were prepared by dissolving plutonium hydroxide in concentrated nitric acid. Pu(VI) solutions were prepared by fuming plutonium solution in perchloric acid to dryness twice and then dissolving the dry mass in nitric acid.

A Cary model 14 recording spectrophotometer was used for recording the spectra.

The spectra of Pu(III), Pu(IV) and Pu(VI) in nitric acid solutions are given in Figs. 38 - 40. Changes occurring with increase in nitric acid concentration in the case of Pu(IV) and Pu(VI) were large owing to their strong complexing tendencies. The molar extinction coefficients were calculated for Pu(III), Pu(IV) and Pu(VI) at major peaks from the optical density values of four different concentrations of plutonium solutions for each of the oxidation state (Tables 40 - 42). The concentration ranges used were: Pu(III) from $2.43 \times 10^{-2}M$ to $3.2 \times 10^{-3}M$; Pu(IV) from $1.51 \times 10^{-2}M$ to $1.4 \times 10^{-3}M$; Pu(VI) from $2.07 \times 10^{-3}M$ to $5 \times 10^{-5}M$. The precision obtained in the estimation varies with the oxidation state with an average RSD of 2.6% for Pu(III), 2.1% for Pu(IV) and 2% for Pu(VI) (Tables 40 - 42).

The method is also useful for determining the total plutonium concentration. A measure of the accuracy of the method for determining the total plutonium concentration was obtained by mixing known volumes of solutions of plutonium in different oxidation states and analysing the resulting mixture for various oxidation states. The experimental concentrations of individual oxidation state were summed up and compared

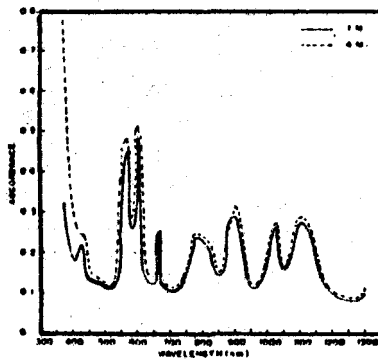


Figure 38 : Absorption spectra of Pu(III) in 1M and 4M HNO₃

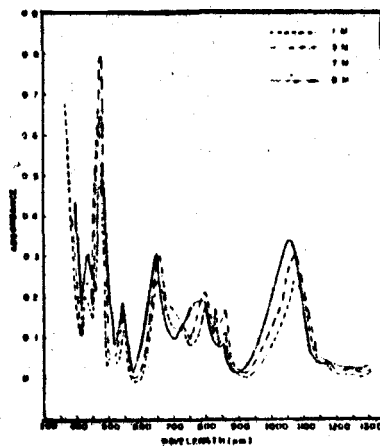


Figure 39 : Absorption spectra of Pu(IV) in 1M, 3M, 7M and 8M HNO₃

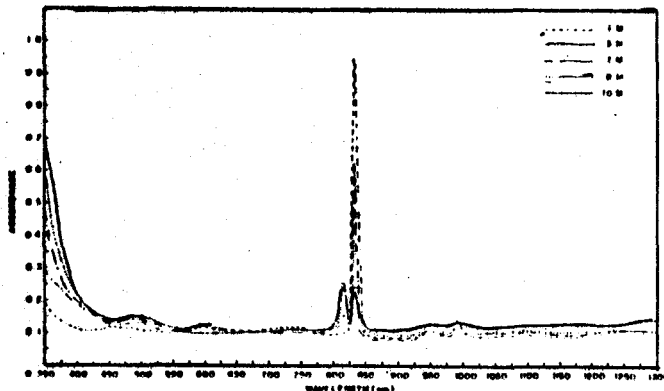


Figure 40 : Absorption spectra of Pu(VI) in 1M, 3M, 8M and 10M HNO₃

TABLE 40

Relative molar absorptivity values of Pu(III) as function of HNO₃ concentration

Molarity of HNO ₃	λ	λ	λ	λ	λ	λ	λ	λ	λ	λ
	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
	567 - 640	603 - 640	567 - Base	603 - Base	831 - 850	477 - 495				
	nm	nm	Line	Line	nm	nm				
	$\bar{\epsilon}$	$\bar{\epsilon}$	$\bar{\epsilon}$	$\bar{\epsilon}$	$\bar{\epsilon}$	$\bar{\epsilon}$				
1	34.8 ± 0.7	33.8 ± 0.2	36.3 ± 1.5	35.5 ± 1.1	2.9 ± 0.7	2.4 ± 0.40				
2	34.0 ± 1.1	33.2 ± 1.3	35.9 ± 0.5	35.2 ± 0.5	3.5 ± 0.3	2.4 ± 1.0				
3	33.3 ± 0.9	33.1 ± 0.9	35.2 ± 0.8	34.4 ± 0.8	2.9 ± 0.01	3.6 ± 1.3				
4	34.7 ± 0.7	33.9 ± 0.8	36.2 ± 0.3	35.4 ± 0.4	3.3 ± 0.7	3.6 ± 1.6				
Average RSD (%)	2.6	2.4	2.1	2.0	13.1	34.4				

1
%

TABLE 21

Relative molar absorptivity values of Pu(IV) as a function of HNO₃ concentration

Molarity of HNO ₃	Δ 477*	Δ - 495**	Δ 477 - Baseline	Δ 660	Δ 690	Δ 1075***	Δ - 1200	Δ 567	Δ 640	Δ 831	Δ 850
	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
	$\bar{\epsilon}$		$\bar{\epsilon}$	$\bar{\epsilon}$		$\bar{\epsilon}$		$\bar{\epsilon}$		$\bar{\epsilon}$	
1	64.9 ± 2.1		76.9 ± 1.3	17.8 ± 0.6		27.1 ± 1.0		- 17.7 ± 1.2		- 4.5	
3	68.4 ± 0.9		80.1 ± 0.2	18.4 ± 0.8		29.9 ± 1.0		- 19.9 ± 1.3		- 4.5 ± 0.5	
5	58.1 ± 1.1		72.1 ± 1.3	18.7 ± 0.7		28.0 ± 1.1		- 20.3 ± 0.4		- 5.6 ± 0.6	
7	37.7 ± 0.4		49.0 ± 0.8	11.6 ± 0.4		28.3 ± 0.7		- 19.2 ± 0.4		- 1.3 ± 0.2	
8	31.9 ± 0.9		43.4 ± 1.5	9.9 ± 0.7		26.5 ± 1.6		- 18.0 ± 0.7		- 1.0	
10	38.5 ± 0.9		51.9 ± 1.1	9.0 ± 0.3		-		- 14.0 ± 1.0		- 1.0	
Average BSD (%)	2.1		2.7	4.3		4.0		4.7		11.7	

- * - Peak shifts from 477 to 491 nm
- ** - Through shifts from 495 to 520 nm
- *** - Peak shifts from 1075 to 1065 nm.

TABLE 42

Relative molar absorptivity values of Pu(VI) as a function of HNO₃ concentration

Molarity of HNO ₃	$\frac{\Delta}{\text{cm}}$	$\frac{\Delta}{\text{cm}}$	$\frac{\Delta}{\text{cm}}$	$\frac{\Delta}{\text{cm}}$	$\frac{\Delta}{\text{cm}}$	$\frac{\Delta}{\text{cm}}$	$\frac{\Delta}{\text{cm}}$	
	831 - 850	815 - 850	567 - 640	477 - 495	$\bar{\epsilon}$			
1	456.0 ± 7.4	-	8.6 ± 2.4	8.5 ± 3.9				
3	420.9 ± 6.1		6.9 ± 1.4	8.5				
5	320.4 ± 2.3	-	7.1 ± 2.2	8.0				
7	184.3 ± 3.4	27.8 ± 1.0	6.9 ± 1.5	1.9 ± 0.7				
8	125.0 ± 4.5	44.4 ± 0.9	6.0 ± 1.4	7.5 ± 2.3				
10	59.8 ± 1.6	64.4 ± 1.1	-	7.0				
Average RSD (%)	2.0	2.5	25.0	35.9				

TABLE 43
Analytical accuracy

Molarity of HNO_3	Sample Number	Measured plutonium concentrations (10^{-3}M)			Total plutonium conc. (10^{-3}M) (measured)	Sum of individual concs. taken (10^{-3}M)
		Pu(III)	Pu(IV)	Pu(VI)		
1	1	0.92	8.85	Nil	9.77	10.68
	2	0.37	8.62	0.20	9.19	9.22
	3	0.53	10.34	0.18	11.05	11.05
2	4	1.15	3.41	0.04	4.60	4.70
5	5	Nil	2.33	0.25	2.58	2.57
8	6	Nil	2.23	0.48	2.71	2.77
10	7	Nil	0.24	0.78	1.02	1.01
	8	Nil	0.49	0.51	1.00	1.00

with total plutonium (Table 43). This method can be adopted for estimating plutonium in fuel reprocessing solutions.

b) Gamma radiolysis of Pu(IV) and Pu(VI) in nitric acid solutions

In continuation of the studies on the radiolysis of plutonium in nitric acid solutions⁽¹⁾, preliminary experiments were carried out on Pu(IV) and Pu(VI) solutions. Nearly 10^{-3} M solutions of Pu(IV) and Pu(VI) in 3M and 8M HNO₃ were irradiated with ⁶⁰Co gamma radiation up to doses of about 3×10^{19} eV/ml in the presence and absence of air and the spectra of irradiated solutions were taken using a Cary-14 spectrophotometer. The optical densities at 476 nm and 831 nm were found to be the same both before and after irradiation showing that Pu(IV) and Pu(VI) are stable to radiation in 3M and 8M HNO₃ solutions. One irradiation of Pu(VI) in 8M HNO₃ containing 0.1M sulphamic acid was carried out in the presence of air with a view to investigating the effect of radiolytically produced H₂O₂ on Pu(VI). In that case also Pu(VI) was found to be stable to radiation. Further work is planned on the analysis of gaseous products released in the system and on extending the studies to systems containing Fe⁺⁺⁺ ions, nitrous acid and organic materials and to beta and alpha radiolysis in order to obtain more closely to the conditions present in process solutions.

References

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4.2.2 EPR studies of intermediates formed in radiolytic reactions in aqueous medium

P.R. Natarajan, S. Vaidyanathan and M.S. Nagar

EPR studies of intermediates formed in the gamma radiolysis of 0.05M FeCl₃ in 0.16M HCl at 77°K were continued to get experience in sample preparation and transfer and recording the spectra. The intensities of the lines⁽¹⁾ at 3244G, 3275G and 3310G were found to be independent of the Fe⁺⁺⁺ concentration but increased linearly with increase in dose. This spectrum having a doublet of 40G

splitting is assigned to that of OH radical produced from the gamma radiolysis of water⁽²⁾.

Frozen samples of 0.1M U(IV) and U(VI) in 0.8N H₂SO₄ were irradiated by gamma rays to a dose of 1M rad at 77°K and the EPR spectra recorded (Fig. 41).

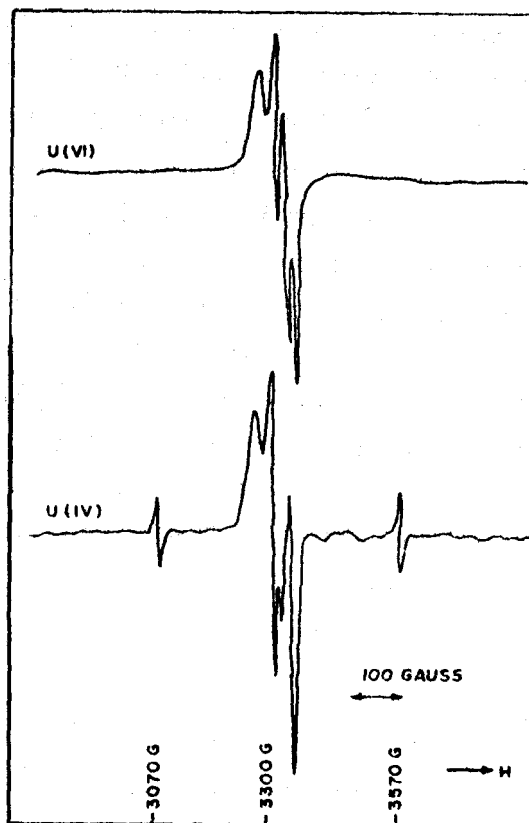


Figure 41: EPR spectra of gamma irradiated frozen samples of U(IV) and U(VI) in 0.8N H₂SO₄.

In both these spectra, the presence of OH radicals was indicated by its characteristic doublet of about 40G splitting. In the U(IV) spectrum the presence of H atoms was also noticed by the doublet with about 500G splitting. The suggested mechanism for the formation of H atoms is by the reaction of mobile electrons with solutes like HSO₄⁻. The absence of H atoms in the U(VI) spectrum may probably be due to the scavenging of the mobile electrons by U(VI).

For carrying out work with plutonium solutions, a quartz dewar flask

similar to the imported one was made. While recording the spectra of plutonium samples, the dewar flask was closed with a teflon stopper, which in turn was connected to the glove box exhaust line through a filter. The arrangement is shown in Fig. 42.

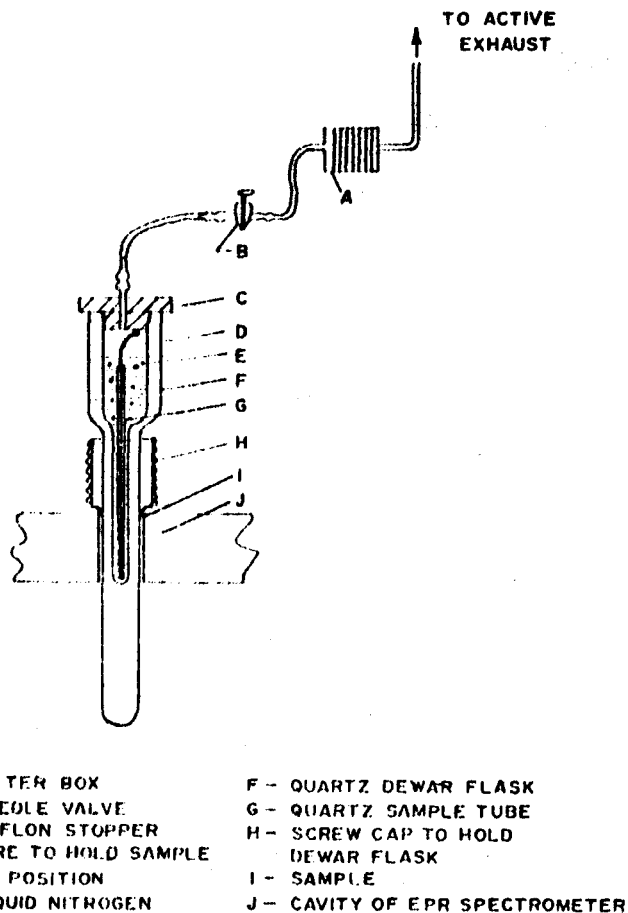


Figure 42: Arrangement for recording EPR spectra of active sample

The EPR spectra of the gamma irradiated (dose 1M rad) frozen samples of 1×10^{-3} M Pu(III) and Pu(IV) in 0.8M H_2SO_4 are shown in Fig. 43. These spectra indicated the presence of H atom and OH radical in these systems. The measurement of yields of these species is in progress. The relative rates of mobile electron reactions with Pu(III) and Pu(IV) will be studied by measuring the yield of H atoms as a function of the concentration of Pu(III) and Pu(IV).

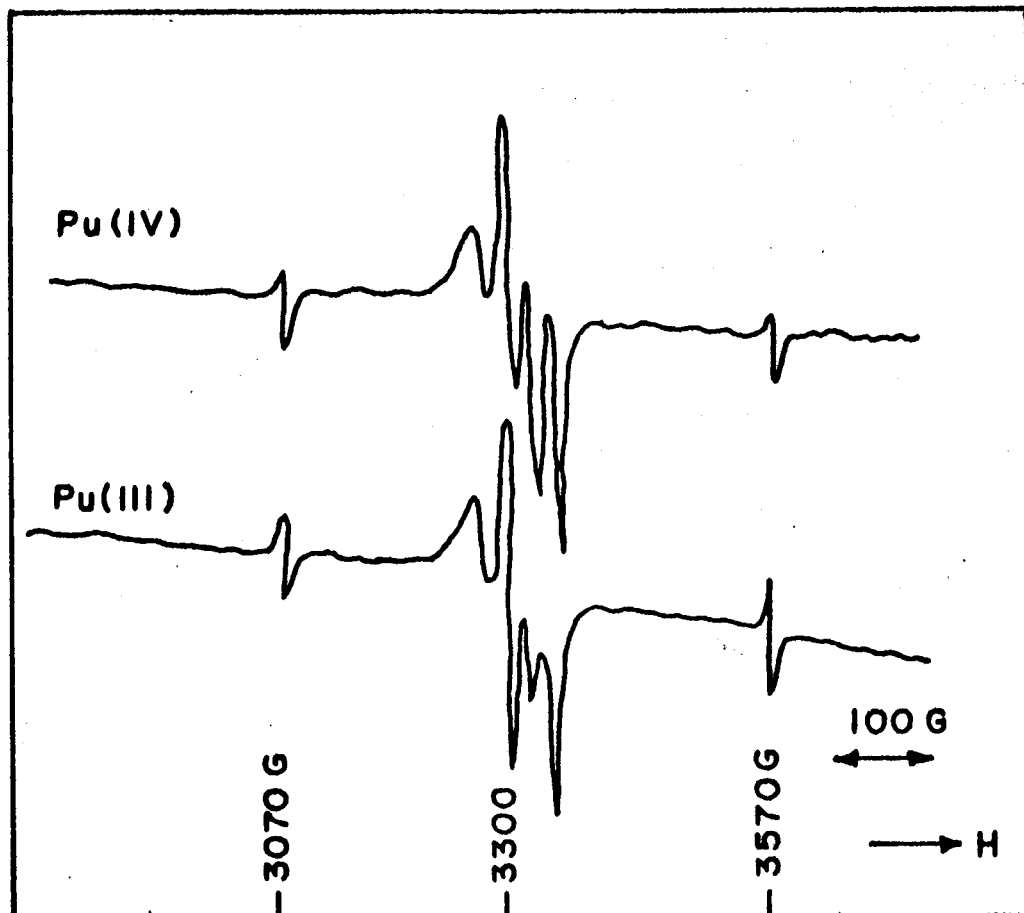


Figure 43: EPR spectra of gamma irradiated frozen samples of Pu(III) and Pu(IV), in 0.8N H_2SO_4 .

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4.2.3 Two phase radiolysis and its effect on the distribution coefficient of plutonium.

P.K. Bhattacharyya, and R. Veeraraghavan

Trilaurylamine (TLA), a long chain tertiary amine is used as an extractant

for plutonium⁽¹⁻⁵⁾ and other actinides^(2, 3) in nuclear fuel reprocessing. The stability of the amine to chemical and radiation effects is, however, not explored under plant conditions⁽⁶⁾. It is, therefore, of interest to study the effects of radiation on the extraction characteristics of the amine in equilibrium with aqueous phase. Some results of the study have already been reported⁽⁷⁾.

Pu(IV) solution was prepared by adding a drop or two of concentrated hydrogen peroxide to a solution of plutonium in 3M HNO₃ and then warming the solution under an infrared lamp for a few minutes. Absence of Pu(VI) in this solution was established by the absence of the characteristic Pu(VI) peak at 831 nm in the absorption spectrum of the solution. Mixtures of Pu(IV) solution and TLA/Xylene were irradiated with gamma rays. The aqueous phase of the system irradiated was 3M HNO₃ containing Pu(IV) in tracer amounts and the organic phase a 2% (v/v) solution of TLA/Xylene solution preequilibrated with 3M nitric acid. Extraction was carried out both in the presence and absence of radiation. The K_d values are given in Table 44. The irradiated amine shows poorer extraction behaviour.

TABLE 44
Variation of K_d value for Pu(IV) with gamma radiation dose

No.	Dose	K _d observed	
		Unirradiated	Irradiated
1	0.4 M rad	296.6	224.0
2	0.8 M rad	287.6	196.3

The absorption spectrum of milligram quantities of Pu(IV) extracted in TLA/Xylene solution from 3M nitric acid was recorded with a Cary-14 spectrophotometer (see Fig. 44). It can be seen that the absorption maximum due to Pu(IV) in organic phase occurs at 493 nm whereas in the aqueous phase the absorption peak is reported to be at 476 nm. The plutonium loaded TLA/Xylene solution was irradiated to a dose of 0.9M rad and it showed no change in the absorbance value at 493 nm. It was, therefore, concluded that Pu(IV) in the organic phase is stable to radiation up to a dose of 0.9M rad.

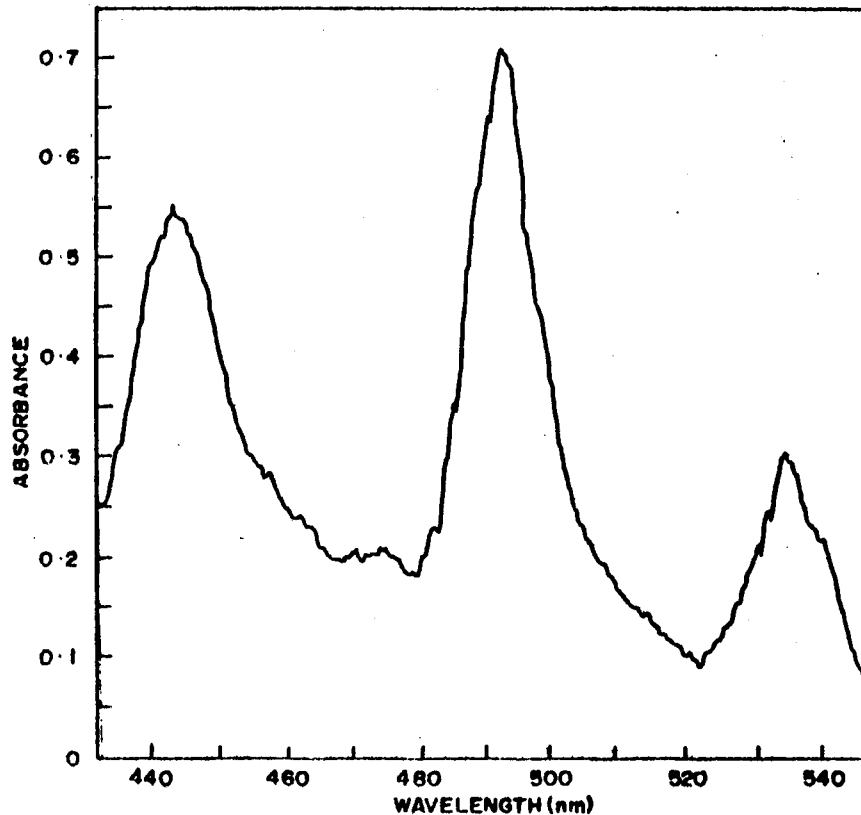


Figure 44: Absorption spectrum of Pu(IV) extracted in TLA/Xylene at 3M HNO₃.

Since, the major radiolytic product of TLA is dilauryl amine⁽⁸⁾, a spectrophotometric method was developed for the ^{its} estimation in presence of TLA. The method was based on the formation of copper salt of dithiocarbamate which absorbs at 440 nm with a molar extinction coefficient 5700 litres mole⁻¹ cm⁻¹.

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4.2.4 Radiation chemistry of nitric acid

P.K. Bhattacharyya and R.D. Saini

Work on the radiation chemistry of nitric acid solutions was continued with a view to understanding the mechanism of radiolysis⁽¹⁾. The effect of OH radical scavengers on $G(\text{H}_2\text{O}_2)$ was investigated to ascertain the role of OH radicals. An attempt was made to separate and identify the end products of the radiolysis by thin layer chromatography.

A method based on interaction of I^- with H_2O_2 and measurement of the absorption of I_3^- ⁽²⁾ was adopted for the measurement of H_2O_2 in the present work. Dose vs. yield curves were obtained for H_2O_2 as shown in Fig.45 and $G(\text{H}_2\text{O}_2)$ was calculated. These values of $G(\text{H}_2\text{O}_2)$ were in agreement with those obtained earlier by a graphical method based on competition kinetics (Table 45).

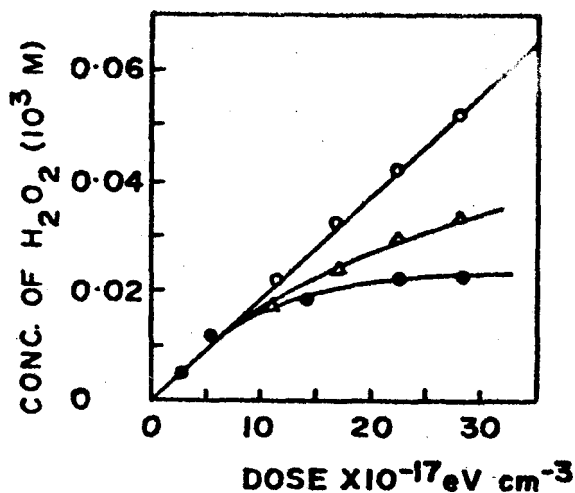


Figure 45: Concentration of H_2O_2 as a function of dose in 1M HNO_3

- : in presence of 1.0 mol m^{-3} sulphanilamide
- Δ : in presence of 4.0 mol m^{-3} sulphanilamide
- : in presence of 20.0 mol m^{-3} sulphanilamide

TABLE 45

G(H₂O₂) values

System irradiated	G(H ₂ O ₂) values Graphical method (3)	G(H ₂ O ₂) values direct determination
0.5M HNO ₃ + SA	0.75	0.80
0.2M " "	0.86	0.81
0.5M " "	0.90	1.07
1.0M " "	0.86	1.10

In the radiolysis of aqueous nitric acid in presence of sulphamylamide (SA), our earlier observations indicated that SA reacts faster than isopropyl alcohol (RCH) with OH radicals to form a transient radical T which gives a nitrocompound designated by TNO₂⁽¹⁾. Spectrophotometric analysis of irradiated solutions showed an absorption maximum at 390 nm which is the region where several nitro-compounds absorb and is different from the absorption maximum of the diazonium compound of SA ($\lambda_{max} = 365nm$). The absorption at 390 nm is ascribed to the compound TNO₂. Since RCH also reacts with OH radicals, the formation of TNO₂ will be suppressed by RCH. Measurements of optical density (O.D.) at 365 nm were carried out on solutions of nitric acid containing RCH and SA and those containing only SA, both irradiated for the same dose. It is seen from Fig.46 that the difference in O.D. of these two solutions ($\Delta O.D.$) is dependent on the ratio of the concentrations of SA and RCH. When the concentration of SA is too small to compete with 10⁻³M RCH for OH radicals, practically all the OH radicals are scavenged by RCH resulting in an increase in the yield of HNO₂^{and} consequently in the amount of diazonium compound by reaction⁽²⁾.



Beyond a concentration of 1.4 x 10⁻⁴ M SA a competition between SA and RCH for OH starts. The effect of RCH on the O.D. decreases with increase of SA concentration. It was not possible, however, to determine k(OH + SA) from the data of Fig.45⁴⁶. However, by employing the method of Rabani and Stein⁽⁴⁾ the rate of constant k(OH + SA) was found to be 3.85 x 10⁹ M⁻¹ Sec.⁻¹.

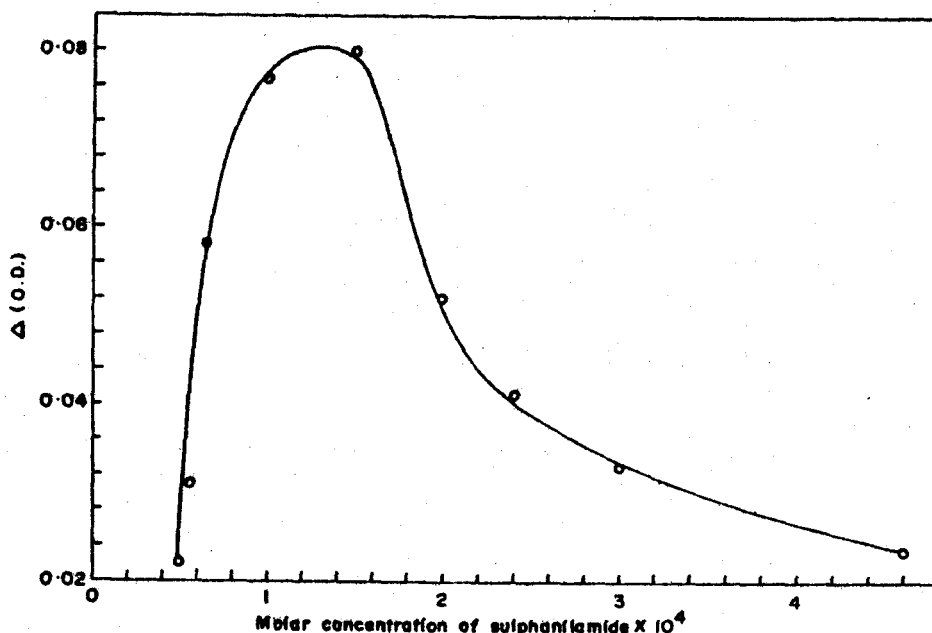


Figure 46: Effect of sulphamylamide in optical density change (Δ O.D.) for HNO_2 produced in the radiolysis of 1M HNO_3 .

In the gamma radiolysis of 0.05M HNO_3 solution containing 0.02M sulphamylamide to a dose of the order of $(1-2) \times 10^{19} \text{ eV g}^{-1}$ a brown precipitate along with a yellowish brown coloured supernatant liquid was obtained. The supernatant liquid after being concentrated on a water bath and neutralized with ammonia gave a brownish white precipitate. The brownish white precipitate was separated and the supernatant liquid was examined by thin layer chromatography using silica Gel 'C' as the coating material and different solvent systems. A solvent system containing ethyl acetate/methanol/25% ammonia solution (17:3:3) showed the presence of more than five components. Identification of the components is in progress with a view to understand the nature of the radiolytic products.

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✓ 4.3 ³⁶⁵² X-ray structural studies

4.3.1 Structural studies on oxalato complexes of uranium(VI)

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Single crystal x-ray studies have shown that in uranyl oxalate $UO_2C_2O_4 \cdot 3H_2O$ the linear uranyl ions have five oxygen atoms coordinated to the uranium atom in a plane perpendicular to the O-U-O axis ⁽¹⁾. This pentagonal bipyramidal configuration is much more stable sterically and geometrically than the postulated hexagonal coordination ⁽²⁾. However, this alone does not lead to any unique structure for other oxalato complexes mainly because of the recent, though limited observation that in all oxalato complexes of actinide elements the oxalate groups are either tri or tetradentate ^(3, 4). The structural studies were, therefore, extended to complex uranyl oxalates.

Bisoxalato dioxodiuranates

The complexes of the general formula $M_2UO_2(C_2O_4)_2 \cdot nH_2O$ were prepared for M = Li, Na, K, Rb, Cs and Tl. The thallium salt $Tl_2UO_2(C_2O_4)_2 \cdot 2H_2O$ was obtained as single crystals suitable for x-ray studies and was, therefore, selected. The results on the thermal decomposition studies of the compound were reported earlier ⁽⁵⁾.

The 0kl, 1kl, and 2kl layers were photographed by the equi-inclination method on a multiple film Weissenberg camera using copper K_{α} radiation and a crystal of approximate dimensions 0.035 x 0.008 x 0.008 cm. The h0l data were obtained on a different crystal. The systematic absences of h00, h odd; 0k0, k odd and 00l, l odd were consistent with the space group $P 2_1 2_1 2_1$.

The intensities were estimated and standard deviations to each of these were