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FORMATION OF FINE SOLID PARTICLES FROM AQUEOUS SOLUTIONS
OF SODIUM CHLOROPALLADATE BY GAMMA-RAY IRRADIATION

October 1994

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Formation of Fine Solid Particles from Aqueous Solutions
of Sodium Chloropalladate by Gamma-ray Irradiation

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Studies have been carried out on the radiation chemical formation of palladium fine particles in argon saturated aqueous solutions of sodium chloropalladate without organic stabilizer. The solutions were irradiated with gamma-rays from a cobalt gamma-ray source and the irradiated solutions were subjected to the dynamic light scattering analysis for the particle diameter measurements, and to the UV-visible optical absorption spectroscopy for the measurements of turbidity (absorption at 700 nm) and remaining chloropalladate ion concentrations in the solution. In the solution of pH = 1.95 by HCl, the turbidity increased after the irradiation and then decreased with time. The concentration of remaining palladate ion in the solution decreased by the irradiation, but it gradually increased with time after the irradiation. These phenomena were qualitatively explained by the reaction scheme in that a precursor to the solid particles still exists in the solution after the irradiation was terminated, and that intermediates including the precursor reacted with chloride ion to re-form chloropalladate ions. The average diameter of the particles after the irradiation was ca. 20 nm and it increased with time to 40 nm at 2.75 kGy, and to 80 nm at 8.25 kGy absorption of radiation. The solution of pH = 0.65 by HCl was found to give lower yields of particles than those observed for the solution of pH = 1.95, and to give the particles of diameters about 150-200 nm. In the solution containing HClO₄ instead of HCl, palladium particles were also formed by the irradiation, whereas no backward reaction after the irradiation was observed due to the

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low concentration of chloride ion in the solution. The average diameter of the particles after the irradiation was about 300 nm and increased with time after the irradiation to a final values which was found to depend on pH of the solution and dose.

Keywords: Palladium Particles, Dynamic Light Scattering, Chloropalladate Ion, γ -ray, Irradiation

塩化パラジウム酸ナトリウム水溶液の γ 線照射による微粒子固体の生成

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(1994年9月20日受理)

アルゴンで飽和した、安定剤を含まない塩化パラジウム酸ナトリウム (Na_2PdCl_6)水溶液を γ 線照射し、生成した粒子の粒子径について動的光散乱装置を用いて、また生成量を可視紫外分光光度計を用いて測定を行った。pH 1.95 HCl 溶液では、濁度 (700 nm における吸光度) は照射終了後、増加しその後減少した。また、238 nm で測定した吸光度から求めた残存 PdCl_4^{2-} は照射により減少したが、照射終了後の時間経過とともに、一部回復することが認められた。これらの現象は、照射終了後も長寿命の前駆体が溶液中に存在し、これらから、微粒子が生成すること、及び一旦生成した同じ或いは別の種類の前駆体が溶液中の塩素イオンとの逆反応により、 PdCl_4^{2-} を再生することが考えられる。粒子径は、照射直後の 20 nm から、時間とともに成長して、線量に依存して、2.75 kGy では約 40 nm、8.25 kGy では約 80 nm に達した。pH 0.65 HCl 溶液では、収量は pH 1.95 の場合に比べて低く、また得られた粒子の粒子直径は、150-200 nm と大きなものであった。HCl の代わりに HClO_4 を用いた溶液では、塩化物イオン濃度が小さいために、逆反応による PdCl_4^{2-} の再生は観測されなかった。照射直後の粒子径は約 300 nm であったが、照射後の時間とともに成長した。最終の粒子径は、線量、溶液の pH に依存することがわかった。

Contents

1. Introduction	1
2. Experimental	1
3. Results and Discussion	2
3.1 Palladate Complexes Present in the Solutions	2
3.2 Absorbance and Concentration of the Solutions	3
3.3 Solutions of pH = 1.95 with HCl	4
3.4 Solutions of pH = 0.65 with HCl	9
3.5 Solutions of pH = 1.95 with HClO ₄	11
3.6 Solutions of pH = 0.65 with HClO ₄	12
3.7 Particle Diameter, Turbidity, and Scattering Intensity	15
3.8 Yields of Solid Particles in HCl and by HClO ₄	15
4. Conclusions	16
Acknowledgement	17
References	17
Appendix	39

目 次

1. はじめに	1
2. 実 験	1
3. 実験結果と考察	2
3.1 塩酸と過塩素酸水溶液中の塩化パラジウム酸イオンの種類	2
3.2 溶液濃度と吸光度	3
3.3 pH = 1.95 塩酸水溶液	4
3.4 pH = 0.65 塩酸水溶液	9
3.5 pH = 1.95 過塩素酸水溶液	11
3.6 pH = 0.65 過塩素酸水溶液	12
3.7 粒子径, 濁度, 及び散乱光強度	15
3.8 塩酸及び過塩素酸水溶液における固体微粒子の収量	15
4. 結 論	16
謝 辞	17
参考文献	17
付 録	39

1. INTRODUCTION

In the previous papers [1, 2], we reported that palladium particles were formed in deaerated palladium sulfate aqueous solution by gamma ray irradiation and that the particles grow during irradiation and after irradiation as well. The estimated density of the particle formed after 1 kGy irradiation is 3 and average diameter of the particles is about 200nm, indicating that the particles are loosely combined palladium atoms or clusters with water molecules. However, we could not observe clusters which are reported to have absorption maximum at about $\lambda = 308$ or 386nm experimentally [3] in the presence of organic stabilizer and at $\lambda = 220$ nm theoretically [4].

Since it is reported that the presence of sulfate ion resulted in rapid disappearance of palladium cluster [3], we have carried out gamma ray irradiation on aqueous solution of sodium chloropalladate instead of palladium sulfate in order to know whether it is possible to observe palladium clusters, and irradiation effects have been studied by UV spectrophotometry and dynamic light scattering (DLS) technique.

There are six different chloro-aquo complexes of different n's; $[\text{PdCl}_n(\text{H}_2\text{O})_{4-n}]^{2-n}$ where $n=0,1,2,3,4$ including cis and trans conformations for $n=2$, depending on $[\text{Cl}^-]$. Reactivities of different ligand configurations of the palladate complex ion are also a subject of the present study.

2. EXPERIMENTAL

The experimental methods were the same as those described in the previous reports [1,2]. Aqueous solutions of pH=1.95 and 0.65 containing 0.3mM sodium chloropalladate were prepared by dissolving solid sodium chloropalladate in corresponding hydrochloric acid and hydroperchloric acid. The solution was deaerated with bubbling argon gas before the gamma ray irradiation, and after the irradiation, the solution was transferred to a cuvette for UV measurements and a cell for dynamic light scattering (DLS) measurements, unless otherwise stated. The doses were from 2.75 to 16kGy.

A few minute after the irradiation, the UV spectrum was intermittently obtained on a Shimadzu UV-3101PC spectrophotometer using time program, creating data files on a disk automatically. After the run, a series of the spectrum data were converted to an absorbance at certain wavelength-time data using a basic program listed in Appendix 1.

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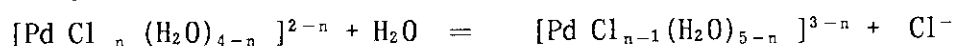
Another few minute later after the irradiation, the photon correlation spectrum was obtained on a DLS apparatus (Ohtuka Electronics Inc., model DLS 600) to obtain scattering photon intensity and diameter of the particles. For the analysis of the data, the UNIMA program which was supplied by the manufacturer and calculated number average particle diameter assuming unimodal distribution of the particle diameter.

3. RESULTS AND DISCUSSION

3.1. Palladate complexes present in the solutions

In Fig. 1A, the spectra of the un-irradiated solutions of pH=1.95 by HCl (a), of pH=0.65 by HCl (b), and pH=1.95 by HClO₄ (c), and 0.65 by HClO₄ (d) are shown, respectively. By comparison of the spectra with those reported (reproduced in Fig. 1B [5]), the spectra were assigned to [Pd Cl_n (H₂O)_{4-n}]²⁻ⁿ of different n's; (a) n=3,2, (b) n=4, and (c) and (d) n=2,3, respectively.

These assignments are confirmed by the following equilibrium considerations: the concentrations of chloro-aquo complexes of different n's can be expressed by the following equilibrium reactions:



$$K_n = ([\text{Pd Cl}_n (\text{H}_2\text{O})_{4-n}]^{2-n}) / ([\text{Pd Cl}_{n-1} (\text{H}_2\text{O})_{5-n}]^{3-n} \cdot [\text{Cl}^-])$$

Rewriting this equilibrium for each step gives the following set of equations:

$$[\text{Pd Cl}_1 (\text{H}_2\text{O})_3]^+ = K_1 [\text{Cl}^-] \cdot [\text{Pd} (\text{H}_2\text{O})_4]^{2+} \quad (1)$$

$$\begin{aligned} [\text{Pd Cl}_2 (\text{H}_2\text{O})_2]^0 &= K_2 [\text{Cl}^-] \cdot [\text{Pd Cl}_1 (\text{H}_2\text{O})_3]^+ \\ &= K_2 K_1 [\text{Cl}^-]^2 \cdot [\text{Pd Cl}_4]^{2+} \quad (2) \end{aligned}$$

$$\begin{aligned} [\text{Pd Cl}_3 (\text{H}_2\text{O})_1]^- &= K_3 [\text{Cl}^-] [\text{Pd Cl}_2 (\text{H}_2\text{O})_2]^0 \\ &= K_3 K_2 K_1 [\text{Cl}^-]^3 \cdot [\text{Pd Cl}_4]^{2+} \quad (3) \end{aligned}$$

$$\begin{aligned} [\text{Pd Cl}_4 (\text{H}_2\text{O})_0]^{2-} &= K_4 \cdot [\text{Pd Cl}_3 (\text{H}_2\text{O})_1]^- \\ &= K_4 K_3 K_2 K_1 [\text{Cl}^-]^4 \cdot [\text{Pd Cl}_4]^{2+} \quad (4) \end{aligned}$$

$$\{[\text{Pd Cl}_4]^{2+}\}_0 = \sum_{n=1}^5 ([\text{Pd Cl}_{n-1} (\text{H}_2\text{O})_{5-n}]^{3-n}) \quad (5)$$

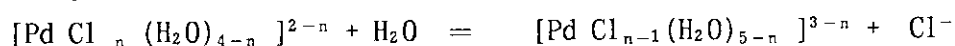
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Rewriting this equilibrium for each step gives the following set of equations:

$$[\text{Pd Cl}_1 (\text{H}_2\text{O})_3]^+ = K_1 [\text{Cl}^-] \cdot [\text{Pd} (\text{H}_2\text{O})_4]^{2+} \quad (1)$$

$$\begin{aligned} [\text{Pd Cl}_2 (\text{H}_2\text{O})_2]^0 &= K_2 [\text{Cl}^-] \cdot [\text{Pd Cl}_1 (\text{H}_2\text{O})_3]^+ \\ &= K_2 K_1 [\text{Cl}^-]^2 \cdot [\text{Pd Cl}_4]^{2+} \end{aligned} \quad (2)$$

$$\begin{aligned} [\text{Pd Cl}_3 (\text{H}_2\text{O})_1]^- &= K_3 [\text{Cl}^-] [\text{Pd Cl}_2 (\text{H}_2\text{O})_2]^0 \\ &= K_3 K_2 K_1 [\text{Cl}^-]^3 \cdot [\text{Pd Cl}_4]^{2+} \end{aligned} \quad (3)$$

$$\begin{aligned} [\text{Pd Cl}_4 (\text{H}_2\text{O})_0]^{2-} &= K_4 \cdot [\text{Pd Cl}_3 (\text{H}_2\text{O})_1]^- \\ &= K_4 K_3 K_2 K_1 [\text{Cl}^-]^4 \cdot [\text{Pd Cl}_4]^{2+} \end{aligned} \quad (4)$$

$$\{[\text{Pd Cl}_4]^{2+}\}_0 = \sum_{n=1}^5 ([\text{Pd Cl}_{n-1} (\text{H}_2\text{O})_{5-n}]^{3-n}) \quad (5)$$

Solving these simultaneous equations using equilibrium constants K_n [5] gives the concentration of chloro-aquo palladate ions at given chloride concentrations, and the results are shown in the following:

[H ⁺]=		Concentration in mM; acid: HCl			
pH	[Cl ⁻]	[PdCl ₁ aq ₃] ⁺	[PdCl ₂ aq ₂] ⁰	[PdCl ₃ aq ₁] ⁻	[PdCl ₄ aq ₀] ²⁻
1.95	0.011	0.01	0.214	0.616	0.16
0.65	0.20	0.00	0.003	0.174	0.82

aq = H₂O

		Concentration in mM; acid: HClO ₄			
pH	[Cl ⁻]	[PdCl ₁ aq ₃] ⁺	[PdCl ₂ aq ₂] ⁰	[PdCl ₃ aq ₁] ⁻	[PdCl ₄ aq ₀] ²⁻
1.95/0.65	0.004	0.057	0.439	0.460	0.04

Equilibrium constants

i	1	2	3	4
K _i	23.7	260	1920	29800

The result indicates that the concentrations of [PdCl₃(H₂O)₁]⁻ and [PdCl₂(H₂O)₂]⁰ are 0.616 and 0.214mM, respectively, when 1 mM of Na₂PdCl₄ was dissolved in pH=1.95 HCl solution. For pH=0.65 HCl solution, the concentrations of [PdCl₃(H₂O)₁]⁻ and [PdCl₄]²⁺ are 0.174 and 0.82mM, respectively. In the solutions of pH=1.95 and 0.65 of hydrochloric acid, only 4 mM of chloride ion which comes from 1 mM sodium chloropalladate is present in the solution, and therefore, the equilibrium concentrations of aquo-rich palladate ions, [PdCl₂(H₂O)₂]⁰ and [PdCl₃(H₂O)₁]⁻ are more abundant than the other systems.

3.2. Absorbance and concentration of the solutions

The UV spectra of aqueous solutions of sodium chloropalladate of different concentrations at pH=1.95 and 0.65 HCl are shown in Figs. 2A and 2B, respectively. The shapes of the spectra obtained for the solution containing different amount of palladate ions were the same in the concentration range shown here if the concentration of chloride ion is the same, indicating that the

relative concentration of aquo-palladate ions of different n 's is regarded to be independent of the concentration of sodium chloropalladate dissolved in the solution as expected by the equilibrium. The UV spectra of sodium chloropalladate of different concentrations at $\text{pH}=1.95$ and 0.65 HClO_4 are shown in Fig. 2C. Both the spectra are quite similar each other, showing that the concentrations of the aquo-chloro palladates of different n ' are almost the same for the two solutions, since the concentration of chloride ion is the same for the two solutions, although hydrogen ion concentration is different.

The absorption at 238nm taken from Fig.2A and that at 280nm taken from Fig. 2B are plotted as a function of concentration in Fig. 3A and that at 236nm from Fig. 2C is plotted in Fig. 3B, which are used for determination of the concentration of the corresponding ions in the solutions.

3.3. Solutions of $\text{pH}=1.95$ with HCl

3.3.1. UV spectra of the irradiated solutions

The spectra obtained immediately after the irradiations of different doses for the solution containing 0.3 mM palladate ion are shown in Fig. 4, where it is noted that (i) absorptions at 208 and 238nm due to palladate ion decreased with increasing dose and disappeared above 8 kGy, and (ii) broad absorption toward longer wave length to 700nm and longer wavelength region (which is not shown in the figure) increased with increasing dose, but above 8 kGy, it decreased with dose. The results show that the palladate ion was consumed by the irradiation and that species absorbing the light in whole wavelength region was formed. The species was assigned as aggregate of metallic character having conduction electron band system which absorbs light of the whole UV and visible region. The absorbance at 238nm and that averaged from 680 through 700nm (referred as turbidity) are taken as the amounts of chloro-aquo palladate ion and those of the metallic aggregate in the solution, respectively.

3.3.2. Turbidity

In Fig. 5A, the absorption at 700nm was plotted as a function of time after irradiation at different doses for the solution initially containing 0.3 mM

palladate ions. The absorption increased with time after irradiation and then decreased with time, except the curve obtained at 11 kGy irradiation which decreased monotonously with time. The increase of the absorption indicates that precursors, possibly, small size clusters of a few palladium atoms, which do not absorb light at 700nm, combined together to form particles which absorb light at 700nm. The decrease of absorption at 700nm indicates that the particles go to sedimentation by further coagulation.

3.3.3. The amounts chloro-aquo palladate

In Fig. 5B, the absorption at 238nm was plotted as a function of time after the irradiation obtained for the same solutions irradiated with different doses as described in the previous section. The absorption at time 0 decreased with irradiation dose indicating that the palladate ion decreased with dose as mentioned before. It is noted that the absorption increased with increasing time. This means that some product formed from the palladate, possibly cluster, reacted backwards with chloride ion to form palladate ions. The rate of backward reaction was highest for the solution irradiated by 5.5 kGy. This may qualitatively be explained by that at low dose, the rate is small since the amount of the cluster is small, and at high dose, the rate also becomes small since the clusters had been combined to form large particles which no longer reacted to form palladate ions.

3.3.4. Photon scattering intensity

Figure 5C shows the photon scattering intensity as a function of time after the irradiation for the solutions (initial concentration of palladate ions: 0.3 mM) irradiated with different doses. At low doses, the scattering intensities are low and seem to increase with time (although measurements were discontinued in the low dose data). At 11 kGy irradiation, the scattering intensity decreased with time. These results are contradict to the results of turbidity measurements (Fig. 5A) where turbidity decreased except for initial period. The explanation for this is not known, but increase of the particle size (see 3.3.5.) may contribute the scattering intensity by $\propto r^6$ [6].

3.3.5. Average particle diameter

Average diameter was plotted as a function of time in Fig. 5D for the

solutions (initial concentration of palladate ions: 0.3 mM) irradiated with different doses. The particles of the smaller diameter were obtained for solution with the smaller dose, and the average diameter gradually increased with time after the irradiation. For example, the diameter is about 15nm after 2.75 kGy, and after 22 hours, the particles grow to 40nm. This means that the the particles formed in the solution combined to grow larger particles possibly by mutual get-together agglomeration even after the irradiation, and possibility of growth of the particle by reducing chloro-aquo palladate ions, because the concentration of these ions did not decrease but increased after the irradiation. The rate of the growth is not in the order of dose, and the rate seems higher for the solutions irradiated with 3.2 or 5.5 kGy. In the solution irradiated with 11 kGy, no increase of the diameter of the particles was observed, possibly because the particle growth terminated during long irradiation period.

3.3.6. Turbidity with or without oxygen

The turbidity (absorption at 700nm) was plotted as a function of time after irradiation (5.3 kGy) in Fig. 6A for (i, ●) the solution (initial concentration of chloro-aquo palladate ion = 0.3mM) saturated with nitrogen before the irradiation, transferred to a cuvette after irradiation in nitrogen atmosphere, and measured with a cover on the cuvette; (ii, ■) solution saturated with nitrogen, transferred to a cuvette in air and measured with a cover on the cuvette; (iii, ◆) saturated with air, transferred to a cuvette in air, and measured without a cover on the cuvette; (iv, ▲) saturated with oxygen before the irradiation, transferred to a cuvette in air, and measured without a cover on the cuvette.

In case (i), the turbidity increased a little after the irradiation, and then gradually decreased (●), indicating the presence of clusters that grow to particles by agglomeration without oxygen, but in case (ii), the turbidity decreased monotonously with time (■) indicating that the clusters were consumed by the presence of oxygen that was dissolved when the solution was exposed to air after the irradiation.

When the solution was saturated with air or oxygen before the irradiation, the formation of the particles decreased to 1/9 and 1/60, respectively, as was observed for the palladium sulfate solution [1]. The decrease of the formation

of the particles can be explained by the two competing reactions; one, solvated electron with chloro-aquo palladate ions, and the other, solvated electron with oxygen, the product of the latter reaction, O_2^- may not be reactive enough to reduce palladate aquo complexes.

The above results well correspond to the absorption at 238nm (Fig. 6B) which can be converted to the concentration of chloro-aquo palladate ions in mM by dividing the molar extinction coefficient of the ions ($\epsilon = 5.43 \text{ mM}^{-1}$). For solution (i, ●), the absorption at 238nm decreased by about 1/5 by the irradiation, and it gradually increased with time after the irradiation, indicating that chloro-aquo palladate re-formed by backward reaction involving chloride ion and un-identified precursor containing palladium in an unstable state. When the solution was exposed to air for short time(ii, ■) during the transfer of the solution from an irradiation test tube to a cuvette, gradual increase of chloro-aquo palladate ions as observed in solution (i) after sudden increase of the chloro-aquo palladate ions was observed. It is suggested that un-identified species which reacts to re-produce palladate ions in solution (ii) is responsible for the gradual increase of turbidity at early period after irradiation in solution (i). In the solutions containing oxygen during the irradiation, the decrease of absorption at 238nm was 1/3 and 2/3 of the initial value (before the irradiation, it was 1.635) for(iii, ◆) air saturated solution and for (iv, ▲) oxygen saturated solution, respectively, as a result of competing reaction of solvated electron or hydrogen atom between oxygen and chloro-aquo palladate ions.

Photon scattering intensity as a function of time after the irradiation is shown in Fig. 6C. For solution(i, ●), the photon intensity increased a little and then decreased with time gradually. For solution (ii, ■) and solution (iii, ◆), the intensity decreased rapidly during short period after the irradiation, and then gradually decreased with time. The behavior found for the three solutions are not much contradict to that of turbidity mentioned above. Photon scattering intensity was very low to allow particle diameter measurement for solution (iii, ◆).

Average diameter of particles as a function of time after the irradiation is shown in Fig. 6D. For solution(i, ●), the diameter increased with time, indicating "get-together" growth of the particles. But it is hardly understood that for solution (ii, ■), diameter is almost constant, and even in the level

smaller than that for solution (iii, ◆).

3.3.7. Agitation and the particle growth

Effects of agitation on the particles in the solutions (initial concentration of palladate ions: 0.2 mM) with or without exposition to air are shown in Fig. 7A, where the turbidity is plotted against time after the irradiation for (i, ●) the solution saturated with argon before the irradiation, transferred to a cuvette after irradiation in nitrogen atmosphere, measured with a cover on the cuvette under agitation with a magnetic stirrer; (ii, ○) solution saturated with argon, transferred to a cuvette in nitrogen, measured with a cover on the cuvette without agitation; (iii, ■) solution saturated with argon, transferred to a cuvette in air, measured without a cover on the cuvette with agitation.

A small increase of turbidity due to the growth of clusters was observed before it decreased with time for case (i), while the decrease of the turbidity is rapid for the case (ii). The reason of the rapid decrease of turbidity by the agitation may be that the agitation encourages aggregation of particles or squeezes out of water molecules from bulky structure of palladium particles. The turbidity decreased more rapidly when the solution was agitated under exposure to air. Excess exposure to air might result in rapid agglomeration.

Absorption at 238nm is plotted as a function of time in Fig. 7B for the three cases, where it is noticed that the plots come to almost the same line for the three cases. This means that a reactant of the re-produced chloro-aquo palladate is not affected by both agitation or exposure to air, but we can not make exact identification of the reactant.

3.3.8. Palladate concentration and properties of particles

In Fig. 8A, the turbidity as measured by the absorption (O.D.) at 700nm is plotted as a function of time after the irradiation (dose: 5.3kGy) for solutions of different concentrations of chloro-aquo palladate ions; 0.1, 0.15, 0.20, 0.25, and 0.3 mM. A series of similar curves were obtained for the solutions except for that of 0.3 mM. These curves, including the last one, show common feature that observed for the oxygen free solutions, i. e., small increase of turbidity due to the formation of non-transparent particles by agglomeration of

clusters. The curves shifted to lower turbidity as the concentration decreases.

In Fig. 8B, absorption (O.D.) at 238nm is plotted as a function of time after the irradiation for the solutions of different concentrations of chloro-aquo palladate ions. A series of similar curves were obtained for the solutions; the absorption decreased to almost zero except for the 3mM solution from the initial values (not shown in the figure, but one can calculate by multiplying concentration by 5.43 mM^{-1}) and then increased with time after the irradiation. The results indicate that most of chloro-aquo palladate ions was consumed by the 5.3 kGy absorption of radiation, but after the irradiation, the chloro-aquo palladate ions recovered by backward reaction, the rate of the reaction depending on the initial concentration of chloro-aquo palladate ions. For the 3mM solution, about 4/5 of the initial amounts of chloro-aquo palladate ions was reacted by the irradiation and then the amounts of the palladate increased with time as for the solutions of the other concentrations.

In Fig. 8C, scattering photon intensity was plotted as a function of time after the irradiation (dose: 5.3kGy) for the solutions of different concentrations of chloro-aquo palladate ions. Plots scattered along lines which decay with time, but dependence of concentration on the plots cannot be recognized.

In Fig. 8D, average diameter of particles is plotted as a function of time after the irradiation (dose: 5.3kGy) for solutions of different concentrations of chloro-aquo palladate ions. A series of similar curves were obtained for the solutions, indicating that the diameter of the particles increased with time after irradiation, the rate of increase of diameter and the diameter of the grown particle are higher and larger, respectively when the initial concentration of the palladate ions are higher. This result can be understood if one consider that the number of particles to undergo mutual agglomeration are larger when the initial concentration is higher. However, the relation is reversed for the 0.1 and 0.15 mM solutions.

3.4. Solutions of pH=0.65 with HCl

3.4.1. UV spectra of the irradiated solutions

The spectra obtained immediately after the irradiations of different doses for the solution (initial concentration of palladate ions: 0.3 mM; defined as (b) in 3.1.) are shown in Fig. 9, where it is noted that (i) absorptions at 223 and 280nm due to palladate ion decreased with increasing dose but did not disappear by 16 kGy, and (ii) broad absorption toward longer wave length to 700nm which was observed for solution (initial concentration of palladate ions: 0.3 mM; pH=1.95 by HCl; defined as (a) in 3.1.) was not clearly recognized (see Fig. 4). The results show that a part of the palladate ion was consumed by the irradiation but non-transparent particles were not formed by the irradiation. The absorbance at 280nm and that averaged from 680 through 700nm are taken as the amounts of chloro-aquo palladate ion and those of metallic particle (referred as turbidity) in the solution, respectively.

3.4.2. Turbidity

The turbidity (absorption at 700nm) was plotted as a function of time after irradiation at different doses in Fig. 10A for the solution initially containing 0.3 mM palladate ions (solution (b)) along with the plots obtained for solution (a) for comparison (from Fig. 5A). The turbidity of solution (b) is smaller than those obtained for solution (a), and the turbidity decreased monotonously with time without initial increase of the turbidity which indicates the presence of precursors, possibly, small size clusters of a few palladium atoms, which combined together to form non-transparent metallic particles as mentioned in 3.3.2. The decrease of the turbidity indicates that the particles go to sedimentation by further coagulation.

3.4.3. The amounts of chloro-aquo palladate

In Fig. 10B, the absorption at 280nm was plotted as a function of time obtained for the same solution (solution (b)) of different doses. The absorption at time 0 decreased with irradiation dose indicating that the palladate ion decreased with dose as mentioned before. It is noted that the absorption increased with increasing time. This means that some product formed from the palladate, possibly cluster, reacted backwards with chloride ion to form palladate, as mentioned in 3.3.3. for solution (a) of pH=1.95. The concentrations of the palladate ions reached equilibrium values faster than those observed for solution (a) (see Fig. 7) and the amounts of palladate ions recovered are about 0.033mM (about 11% of the initial amounts of the palladate

ions), and are not much different for solutions irradiated with different doses.

3.4.4. Diameter and photon scattering intensity

Photon scattering intensity was weak for the solution (b) and decayed quickly with time as shown in Fig. 10C. Therefore, observation of diameter was only possible for initial 5 hours, and the data was plotted in Fig. 10D, which indicates the presence of 200-300nm particles the solutions. The results may be explained by that most of the large particles were precipitated leaving smaller particles in the solution.

3.5. Solutions of pH=1.95 with HClO₄

3.5.1. UV spectra of the irradiated solutions

The spectra obtained immediately after the irradiations of different doses for the solution (initial concentration of palladate ions: 0.3 mM; defined as (c) in 3.1.) are shown in Fig. 11, where it is noted that (i) absorptions at 208 and 236nm due to palladate ion decreased with increasing dose and disappeared by 16 kGy, and (ii) broad absorption toward longer wave length to 700nm which was observed for solution (concentration of palladate ions: 0.3 mM; defined as (a) in 3.1.) appeared and superimposed on the absorption of the palladate ions to increase over the whole range of spectrum (see the spectrum after 10.6 kGy irradiation). The results show that a part of the palladate ion was consumed by the irradiation and non-transparent metallic particles which have broad absorption in UV-visible range were formed by the irradiation.

3.5.2. Turbidity

Turbidity (absorption at 700nm) was plotted as a function of time after irradiation at different doses in Fig. 12A for the solution (initial concentration of palladate ions: 0.3 mM; defined as (c) in 3.1.). The turbidities after 5.3 kGy and 15.9 kGy decreased monotonously with time without apparent initial increase of the turbidity. However, the turbidity after 10.6kGy shows the initial increase of the turbidity before it decayed, which indicates the presence of precursors, possibly, small size clusters of a few

palladium atoms, which combined together to form non-transparent particles as mentioned in 3.3.2. and 3.4.2. The decrease of the turbidity indicates that the particles go to sedimentation by further coagulation.

3.5.3. The amounts of chloro-aquo palladate

In Fig. 12B, the absorption at 236nm was plotted as a function of time obtained for the same solution (solution (c)) of different doses. The absorption at time 0 decreased with irradiation dose indicating that the palladate ion decreased with dose as mentioned before. It is noted that the absorption decreased after the irradiation and then increased with increasing time a little (for 5.3 kGy) or little increased with time (for 10.3 kGy). This means that some product formed from the palladate, possibly cluster, hardly react backwards with chloride ion to form palladate, because the concentration of chloride ion is small in this solution. After 15.9 kGy, all the palladate ion was reacted to form particles and did not recover with time.

3.5.4. Diameter and photon scattering intensity

Photon scattering intensities were plotted as a function of time in Fig. 12C for the solution(c) irradiated with 5.3, 10.6, and 15.9 kGy. The intensities decreased monotonously with time, showing that the particles precipitate with time. The change of diameter of the particles were plotted in Fig. 12D for the three solutions. For the solutions irradiated with 5.3 and 15.9 kGy, the particle diameter increased rapidly at early period after the irradiation and reached a level-off value of about 900nm, but for the solution irradiated with 10.6 kGy, the particle diameter gradually increased from about 80nm to 400nm.

3.6. Solutions of pH=0.65 with HClO₄

3.6.1. UV spectra of the irradiated solutions

The spectra obtained immediately after the irradiations of different doses for the solution (initial concentration of palladate ions: 0.3 mM; defined as (d) in 3.1.) are shown in Fig. 13, where it is noted that (i) absorptions at

208 and 236nm due to palladate ion decreased with increasing dose as observed in solution (c) (see Fig. 11), and disappeared by 10.6 kGy which is smaller than that observed for solution (c), and (ii) broad absorption toward longer wave length to 700nm which was observed for solutions (a) and (c) appeared and superimposed on the absorption of the palladate ions to increase over the whole range of spectrum (see the spectrum after 5.3 kGy irradiation). The results show that the palladate ion was consumed by the irradiation and non-transparent metallic particles were formed by the irradiation.

3.6.2. Turbidity

The turbidity (absorption at 700nm) was plotted as a function of time after irradiation at different doses in Fig. 14A for solution (d). The turbidities decreased monotonously with time without apparent initial increase of the turbidity. This indicates precursors, small size clusters of a few palladium atoms, which combined together to form non-transparent particles as mentioned in 3.3.2. and 3.4.2. was reacted during irradiation and was not present in the solutions after irradiation. The particles grown up to certain diameter undergo sedimentation resulting observed monotonous decay of turbidity (see 3.6.3, Fig. 14B).

3.6.3. The amounts of chloro-aquo palladate

In Fig. 14B, absorption at 236nm was plotted as a function of time obtained for the same solutions of different doses. For the solution irradiated with 5.3 kGy, the absorption at time 0 decreased to 0.15, indicating that 22% of the initial palladate ions were reacted, and the absorption slowly increased with time. The increase indicates that there was some recovery of the palladate ions due to backward reaction, but the amounts of recovery was small compared to solutions (a) and (b). The absorption at 236nm was practically zero for the solutions irradiated with 10.6 and 15.9 kGy, showing most of the palladate ions were consumed and did not recover after the irradiation.

3.6.4. Diameter and photon scattering intensity

Photon scattering intensities were plotted as a function of time in Fig. 14C for the solution (d) irradiated with 5.3, 10.6, and 15.9 kGy. The intensities decreased monotonously with time as in solution (c), showing that

the particles precipitate with time. Diameter of the particles was plotted in Fig. 14D for the three solutions as a function of time after the irradiation. For the solutions irradiated with 5.3 kGy, the particle diameter increased gradually from 270nm to 1500nm, while in the solutions irradiated with 10.6 and 15.9 kGy, the particle diameter increased rapidly at early period after the irradiation and reached a level-off value of about 800nm.

3.6.5. Supersonic irradiation of the solution

In Fig. 15A, the turbidity was plotted as a function of time for the solution (d) irradiated with 5.3, 10.6, and 15.9 kGy. Among these solutions, the solutions of the latter two were further agitated with irradiation of supersonic wave after most of the particles were precipitated. For the latter solution (i. e., the solution with 15.9 kGy absorption of radiation), the supersonic irradiation was repeatedly made for two more times. The turbidity decay curves of initial 100000 sec are the same data plotted in Fig. 14A. The turbidity increased by the supersonic agitation, and then decreased with time showing a sort of stage after the agitation was discontinued, suggesting that there are fraction of large size particles of uniform distribution [2]. Similar decay curves were obtained after the second and third agitation, but after the fourth, the increase of the turbidity is quite small than the former agitations, perhaps due to coagulation of precipitated particles in the bottom of the cell. Similar result was obtained for the solution absorbed 10.6 kGy radiation dose.

In Fig. 15B, the photon intensity was plotted as a function of time after the gamma-ray irradiation. Every time after most of the suspension was settled down, the solution was irradiated with supersonic waves for one hour, and then the scattering photon intensity was plotted as a function of time. The agitation by supersonic irradiation was repeated for two more times. The intensities after the gamma-ray irradiation and the first supersonic irradiation showed similar decays each other, but after the second and the third, the intensities are lower than those of the former two. This means that as the number of the repeated cycles of sedimentation and re-stirring of the solution increases, the more densely packed particles are formed. The diameter of the particles did not much change after every cycle of precipitation and the supersonic irradiation and the diameter of the particles increased with time.

3.7. Particle diameter, turbidity, and scattering intensity

The change of the particle diameter with time is considered by two contradicted processes; (a-i) increase of the particle diameter by growth of particles by mutual coagulation process (a-ii) increase of the particle diameter by adsorption of small clusters, and (a-iii) apparent decrease of the particle diameter by sedimentation of large particles leaving small particles in the solution. The change of turbidity is considered by (b-i) decrease of turbidity by increase of diameter of particles (b-ii) decrease of turbidity by loss of the particles by sedimentation. Decrease of turbidity due to loss of particles, which is grown enough to absorb light of broad wavelength, by backward reaction to form the palladate ions can be eliminated, since recovery of the palladate ions may be resulted from the reaction of cluster and chloride ion. Scattering intensity reflects the number of particles in solution, but it may also depend on particle diameter and other parameters such as diameter distributions or density, and therefore, we did not consider it for details [7].

3.8. Yields of solid particles in HCl and by HClO₄

In Figs. 16A and B, the turbidities and the concentrations palladate ions are plotted as a function of dose for the four different solutions; (a)pH = 1.95, HCl; (b)pH = 0.65, HCl; (c)pH = 1.95, HClO₄; and (d)pH = 0.65, HClO₄. The turbidities increased and the concentrations of the remaining chloropalladate ions decreased with absorbed dose. The turbidities observed for solutions (c) and (d) are almost the same and higher than solutions (a) and (b), the turbidity of the latter being the lowest. This indicates that the concentration of the chloride ion (see 3.1.) is important for the yield of the solid particles as measured by the turbidity and pH is not. The decrease of the concentrations was smaller for solution (b) than those observed for the other three, indicating that in the solution (b), the backward reaction to re-form chloropalladate ions was most enhanced by the highest concentration of chloride ion. There was not much difference in the decrease of the concentration between solution (a) and solutions (c) and (d).

4. CONCLUSIONS

The irradiation of sodium chloropalladate aqueous solution without the presence of stabilizer produces fine particles. The turbidity which relates to the amounts of fine particles suspended in the solution increased a little immediately after the irradiation, and then decreased with time, indicating that a precursor of the particles were present during a few tens minutes after the irradiation. This phenomenon was not observed for the palladium sulfate solution[7], but was observed for the palladium-silver sulfate solutions[7], because sulfate ion accelerates growth of particles [3] in the former, whereas in the latter solution, reduced silver atoms or clusters will cover the palladium cluster surface to retard the aggregation. The acceleration of the aggregation process due to sulfate ion did not occur in the chloropalladate solutions in the present study where no sulfate ion (which accelerates aggregation of palladium atoms or clusters) is present in the solution, and this allowed us to observe the initial increase of the turbidity due to the precursor.

The amounts of the particles were found to depend on the concentration of chloride ion which reacted with a precursor of the particles to re-form chloropalladate ions. The diameters of the particles formed in the solution also depend on the concentration of chloride ion, dose, and concentrations of the palladate ions, and the average diameter observed for the particles from pH=1.95 HCl solution of 0.3mM chloropalladate was 20nm after the irradiation, and increased depending on the dose absorbed, and was 40nm for 2.75 kGy absorbed dose and 80nm for 8,25 kGy. DLS measurement revealed that average diameter of the particles after irradiation is 50 nm which is smaller than those observed for palladium sulfate solution.

Different results were obtained on the particle diameter, the amounts of particles formed and the amounts of regeneration of palladate ions by the backward reaction for the solutions containing HCl and HClO₄, and the results can be explained by the difference of chloride ion in the two solutions.

In some cases, the amounts of particles and its growth are found not to be very accurate and seem to depend on unknown reaction conditions which will have to be cleared in the following experiments.

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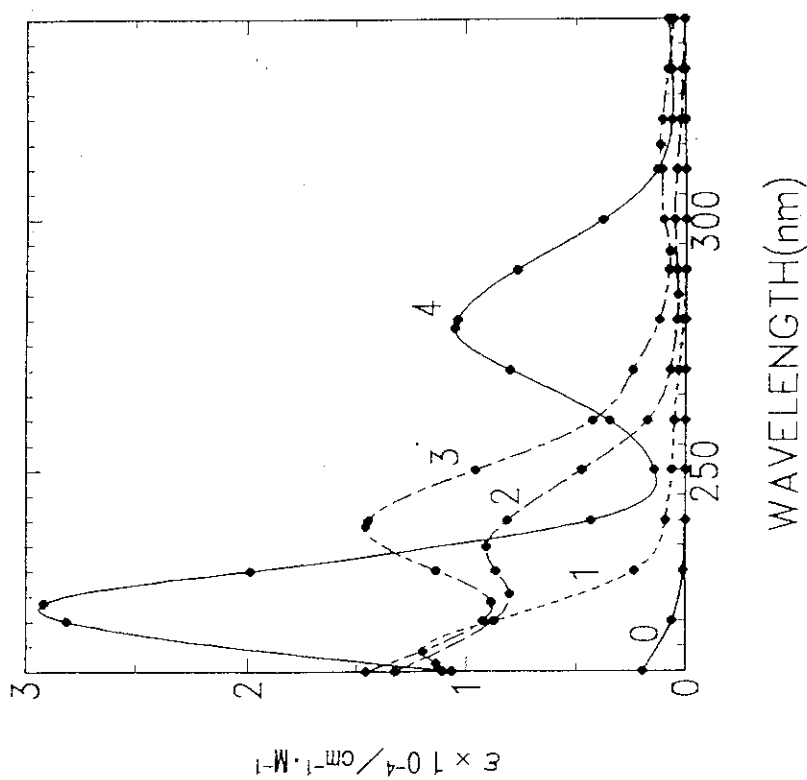


Fig. 1B Electronic spectra of sodium chloro-palladate ions, $[\text{PdCl}_n(\text{H}_2\text{O})_{4-n}]^{2-n}$; (0) $n=0$, (1) $n=1$, (2) $n=2$, (3) $n=3$, (4) $n=4$, [5]

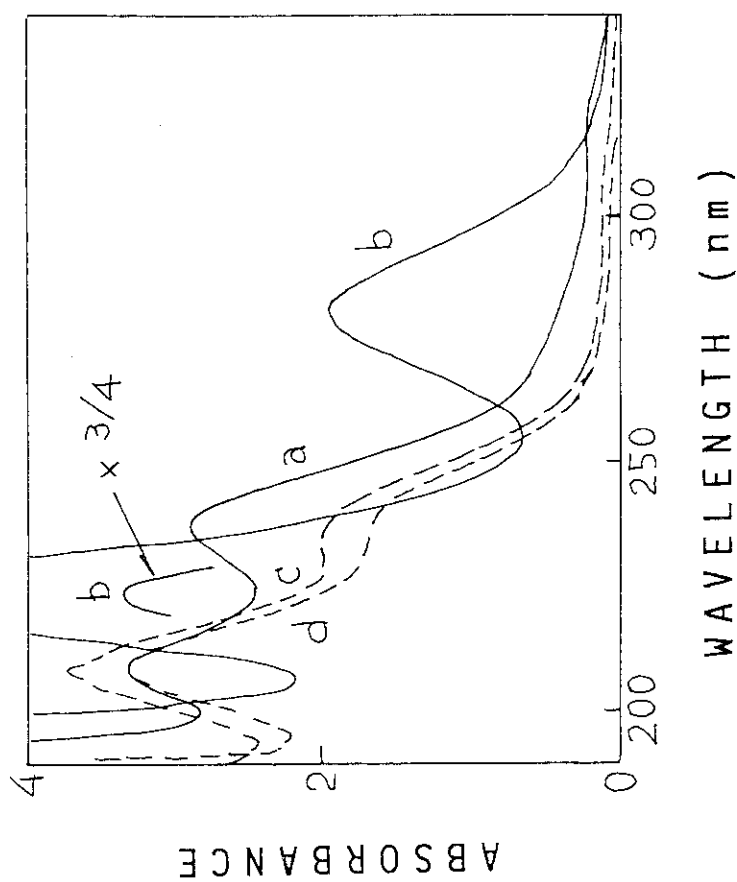


Fig. 1A Electronic spectra of sodium chloro-palladate aqueous solutions; (a) $\text{pH} = 1.95 \text{ HCl}$, (b) $\text{pH} = 0.65 \text{ HCl}$, (c) $\text{pH} = 1.95 \text{ HClO}_4$, (d) $\text{pH} = 0.65 \text{ HClO}_4$.

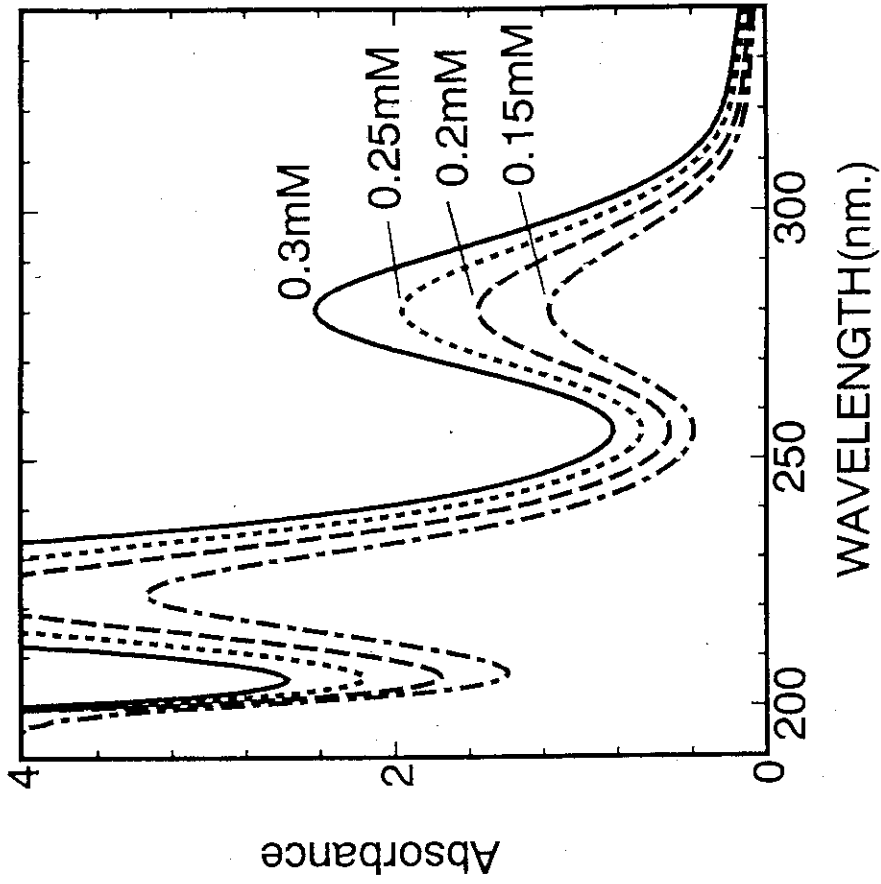


Fig. 2B Electronic spectra of sodium chloro-palladate aqueous solutions of different concentrations; pH = 0.65, HCl.

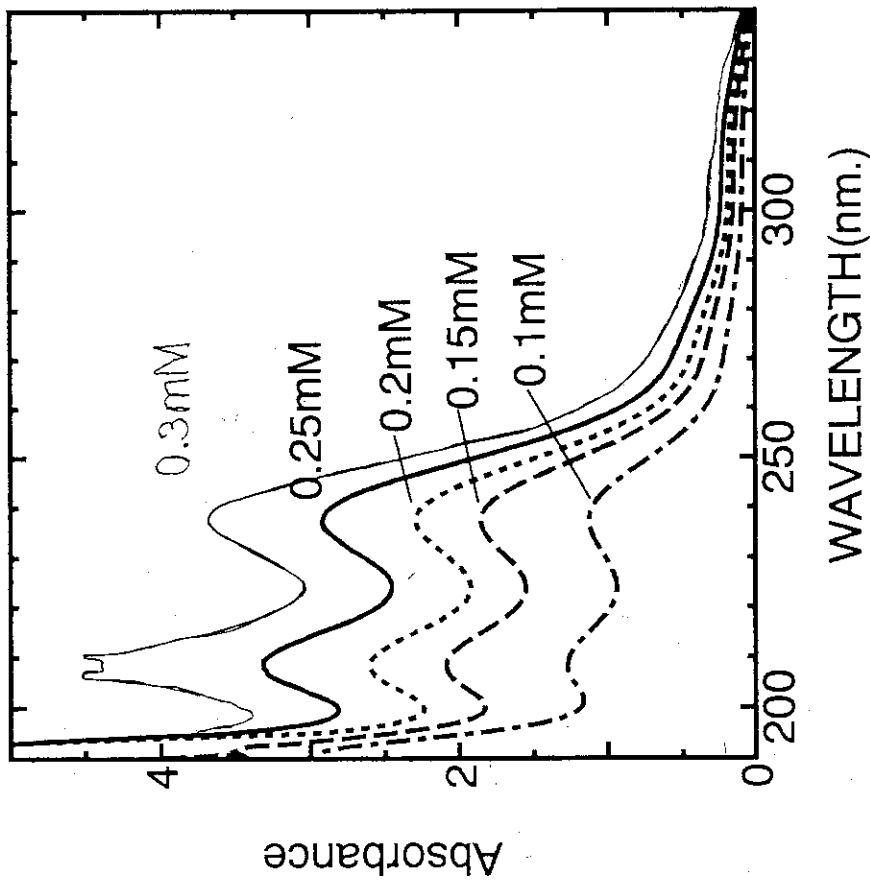


Fig. 2A Electronic spectra of sodium chloro-palladate aqueous solutions of different concentrations; pH = 1.95, HCl.

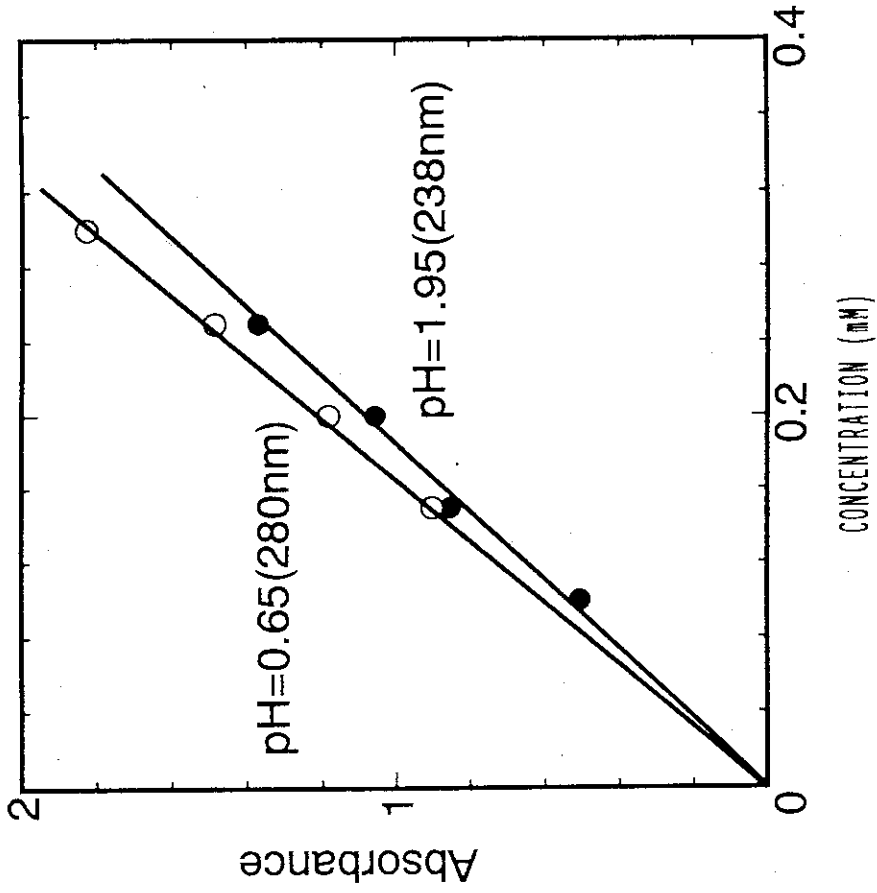


Fig. 3A. Plot of absorbance (O.D.) as a function of concentration of palladate ions; acid: HCl.

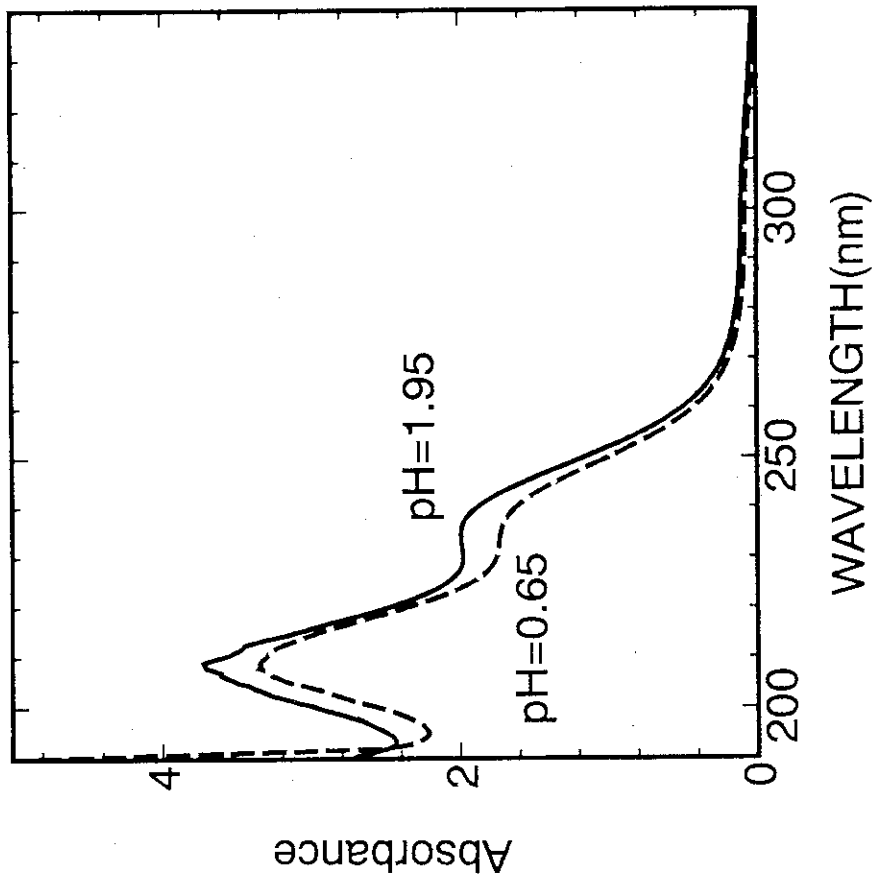


Fig. 2C. Electronic spectra of 0.3 mM sodium chloro-palladate aqueous solutions of different pH's with HClO₄.

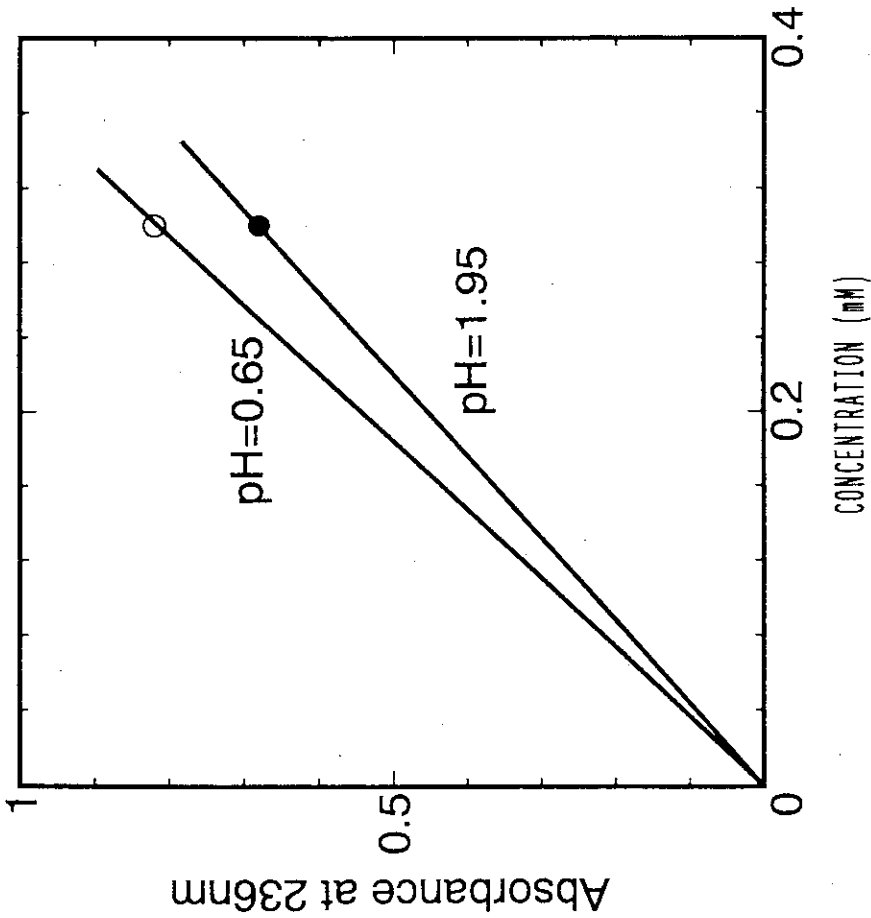


Fig. 3B Plot of absorbance (O.D.) as a function of concentration of palladate ions; acid: HClO₄.

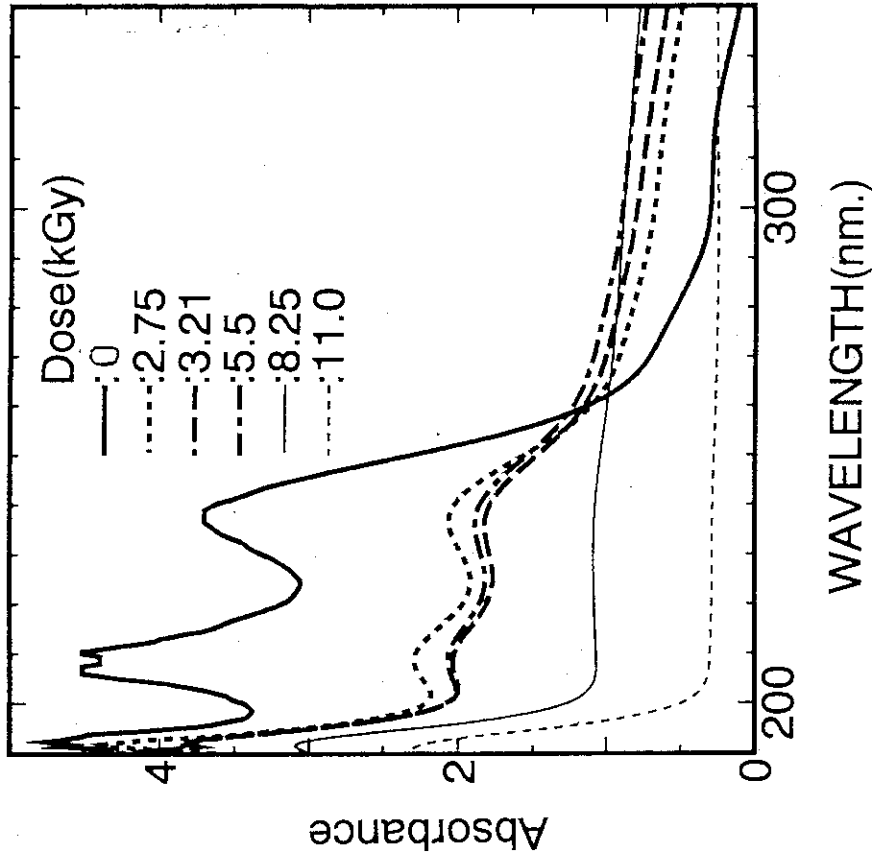


Fig. 4 Electronic spectra of aqueous solution of palladate ions after irradiation of different doses; pH = 1.95, HCl; concentration of palladate ion: 0.3 mM.

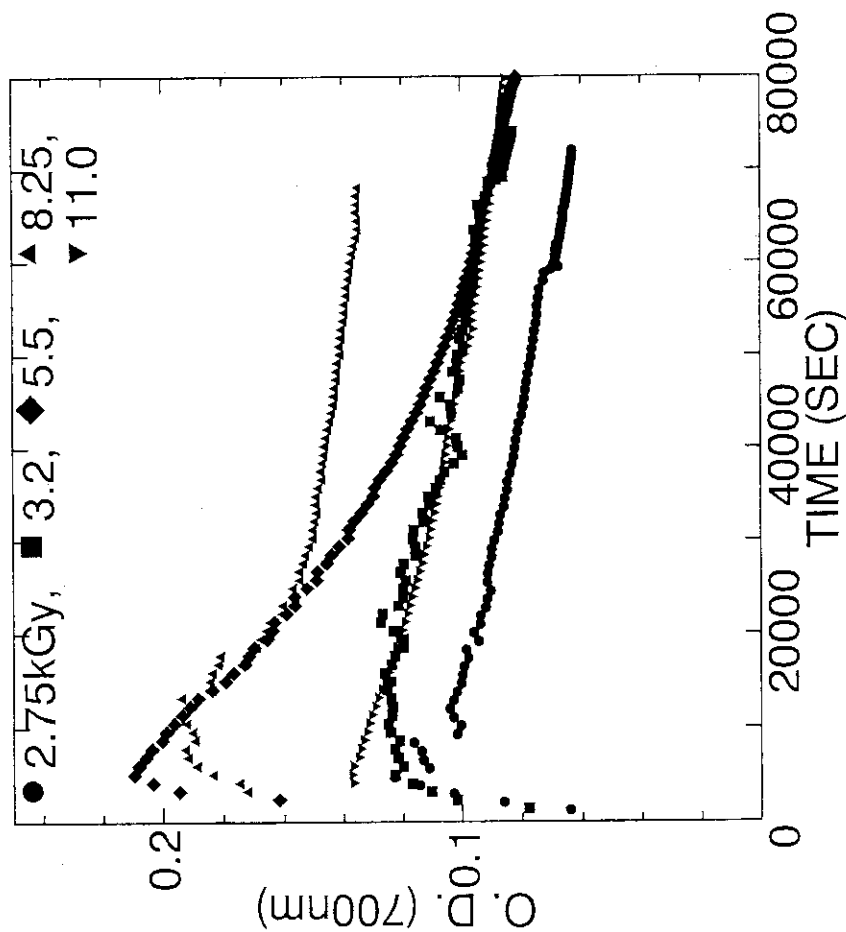


Fig. 5A Absorbance (O. D.) at 700 nm as a function of time for the solutions with different absorbed radiation doses; time zero in the abscissa is the time of initiation of the irradiation; ● : 2.75; ■ : 3.21; ◆ : 5.5; ▲ : 8.25; ▼ : 11.0 kGy; the initial concentration of the palladate ion: 0.3 mM; pH = 1.95 HCl.

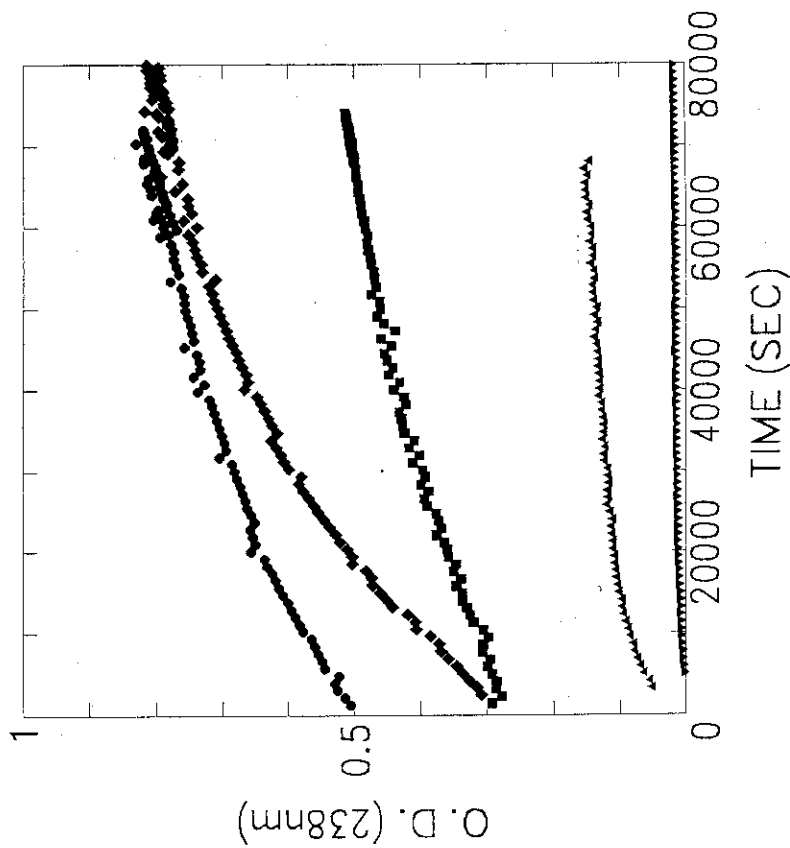


Fig. 5B Absorbance (O. D.) at 238 nm as a function of time for the solutions with different absorbed radiation doses; time zero in the abscissa is the time of initiation of the irradiation; ● : 2.75; ■ : 3.21; ◆ : 5.5; ▲ : 8.25; ▼ : 11.0 kGy; the initial concentration of the palladate ion: 0.3 mM; pH = 1.95 HCl.

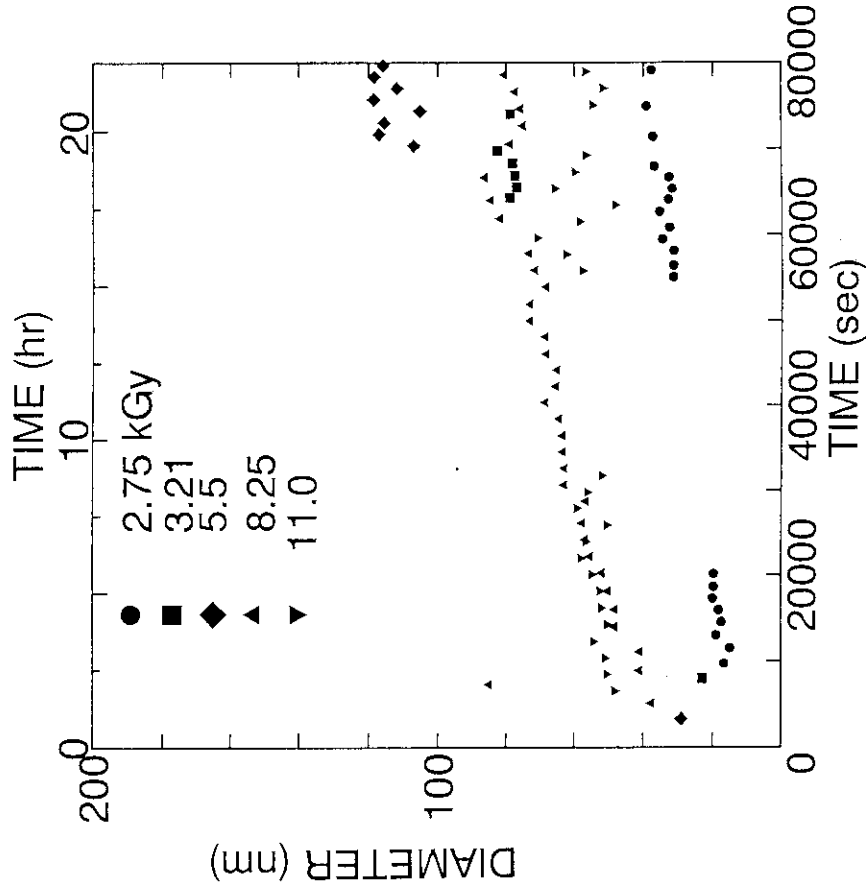


Fig. 5D Average diameter of the particles as a function of time for the solutions with different absorbed radiation doses; time zero in the abscissa is the time of initiation of the irradiation; ● : 2.75; ■ : 3.21; ◆ : 5.5; ▲ : 8.25; ▼ : 11.0 kGy; the initial concentration of the palladate ion: 0.3 mM; pH = 1.95 HCl.

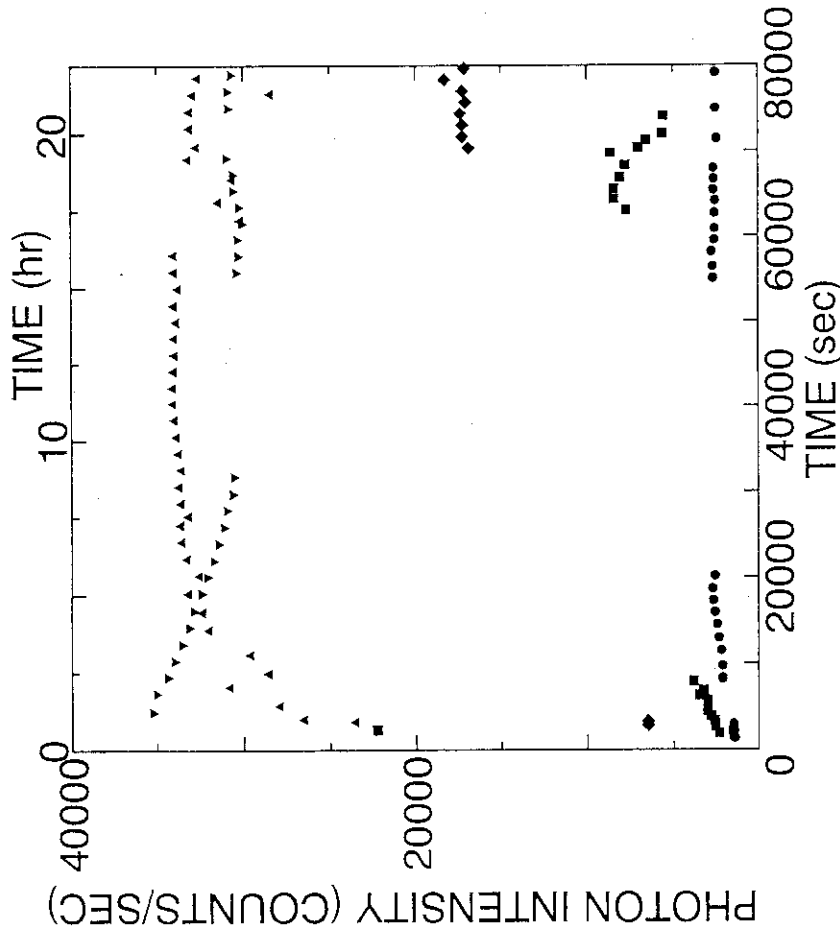


Fig. 5C Scattering photon intensity as a function of time for the solutions with different absorbed radiation doses; time zero in the abscissa is the time of initiation of the irradiation; ● : 2.75; ■ : 3.21; ◆ : 5.5; ▲ : 8.25; ▼ : 11.0 kGy; the initial concentration of the palladate ion: 0.3 mM; pH = 1.95 HCl.

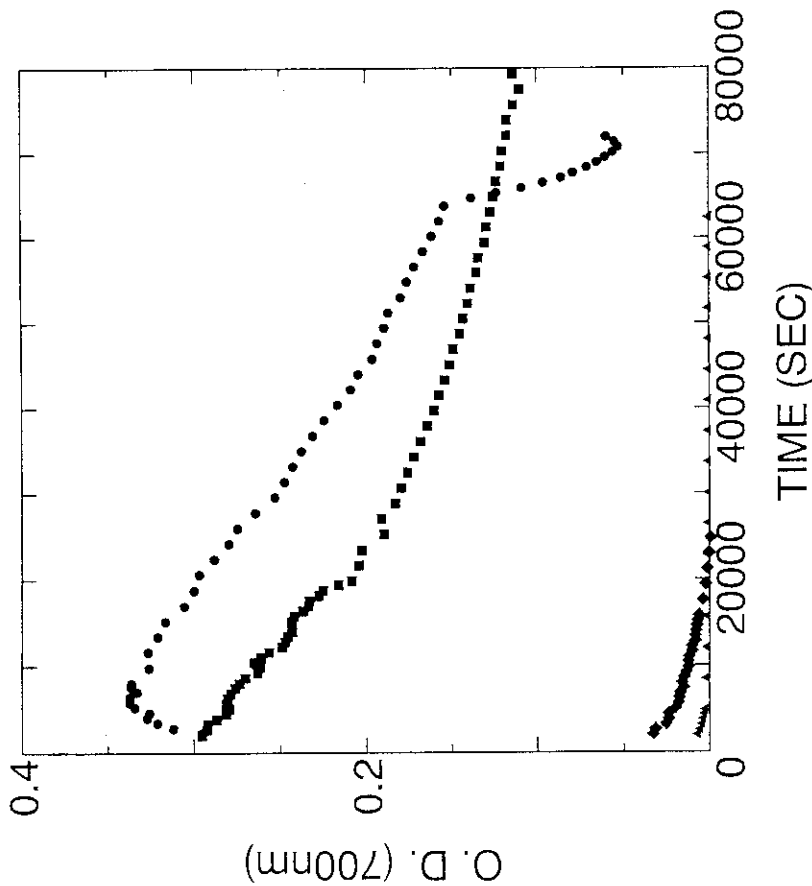


Fig.6A Absorbance (O. D.) at 700 nm as a function of time for the solutions with different absorbed radiation doses; time zero in the abscissa is the time of initiation of the irradiation; ● : no exposure to air; ■ : short exposure to air during sample transfer to cells; ◆ : air saturated solution; ▲ : oxygen saturated solution; the initial concentration of the palladate ion: 0.3 mM; pH = 1.95 HCl. Agitation initiated at 65 ksec resulted discontinuous decrease of O. D. (●).

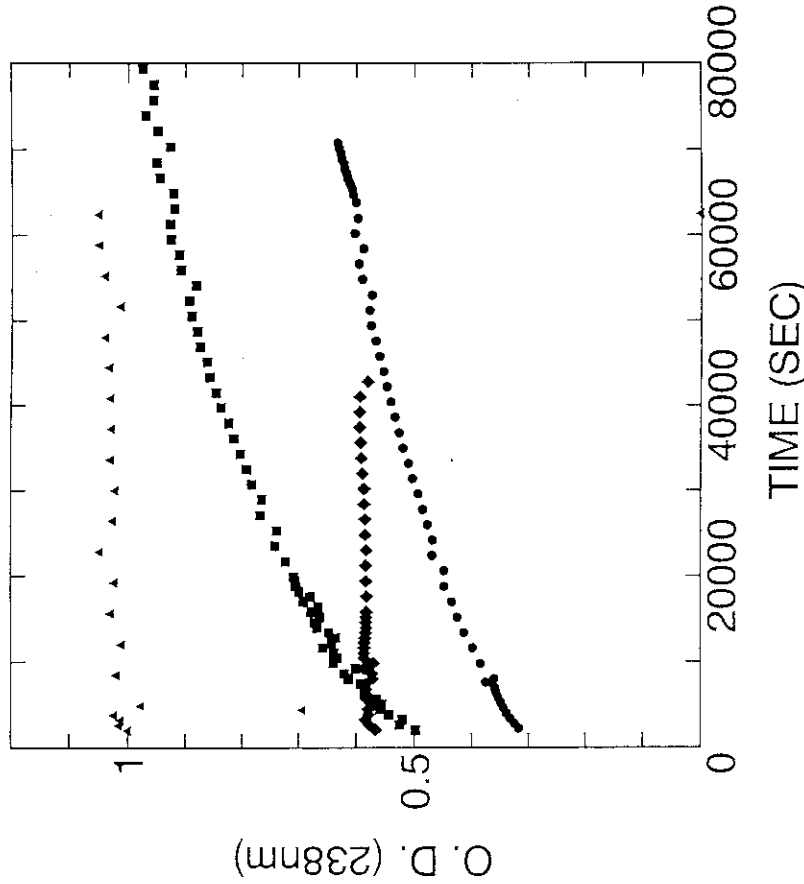


Fig.6B Absorbance (O. D.) at 238 nm as a function of time for the solutions with different absorbed radiation doses; time zero in the abscissa is the time of initiation of the irradiation; ● : no exposure to air; ■ : short exposure to air during sample transfer to cells; ◆ : r saturated solution; ▲ : oxygen saturated solution; the initial concentration of the palladate ion: 0.3 mM; pH = 1.95 HCl.

HCl, pH=1.95, dose:5.3kGy

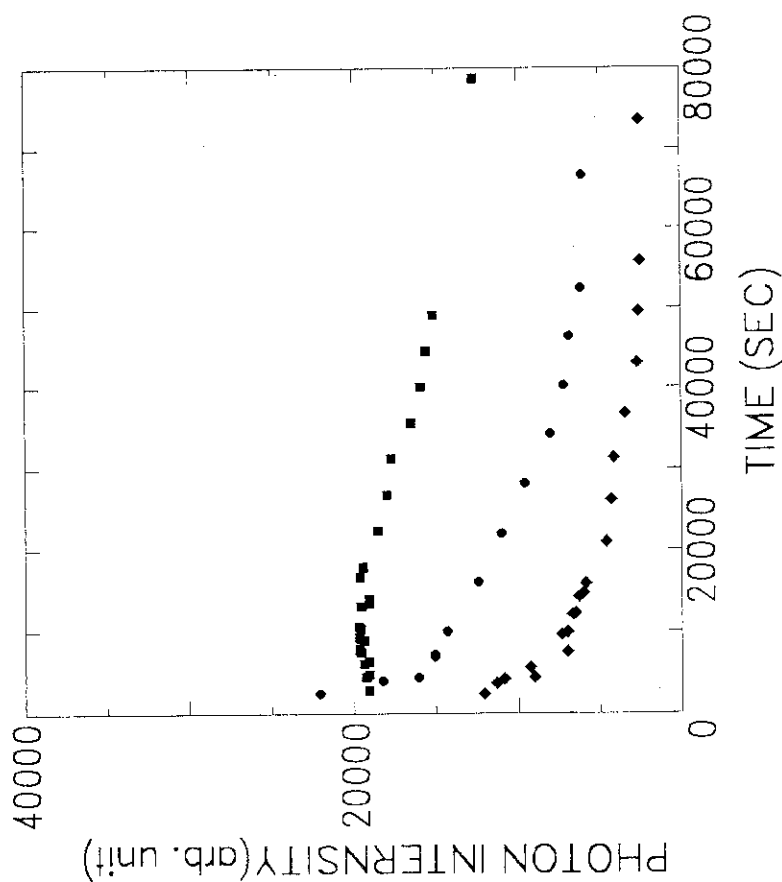


Fig. 6C. Scattering photon intensity as a function of time for the solutions with different absorbed radiation doses; time zero in the abscissa is the time of initiation of the irradiation; ● : no exposure to air; ■ : short exposure to air during sample transfer to cells; ◆ : air saturated solution; the initial concentration of the palladate ion: 0.3 mM, pH = 1.95 HCl.

HCl, pH=1.95, dose:5.3kGy

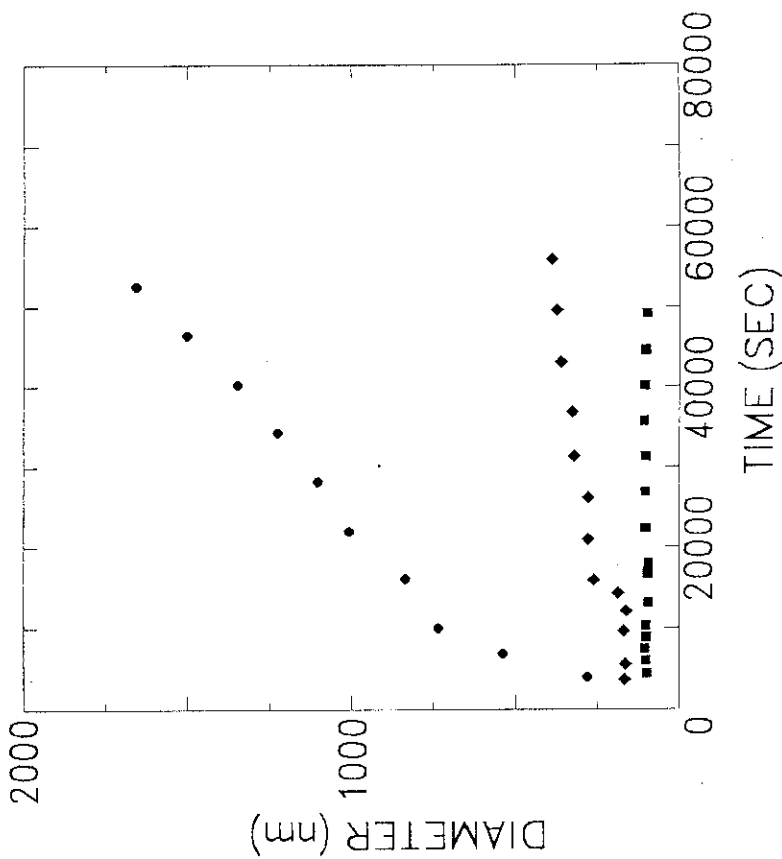


Fig. 6D. Average particle diameter as a function of time for the solutions with different absorbed radiation doses; time zero in the abscissa is the time of initiation of the irradiation; ● : no exposure to air; ■ : short exposure to air during sample transfer to cells; ◆ : air saturated solution; the initial concentration of the palladate ion: 0.3 mM; pH = 1.95 HCl.

HCl, pH=1.95, dose:5.3kGy

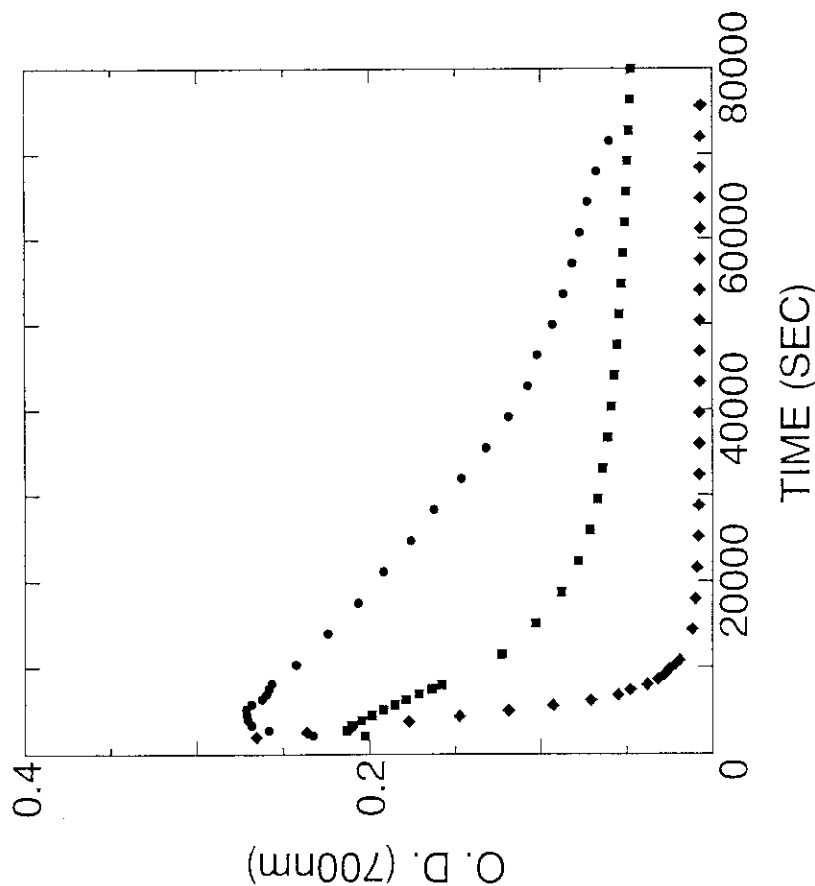


Fig. 7A Absorbance (O.D.) at 700 nm as a function of time for the solutions with or without the presence of oxygen and agitation by a magnetic stirrer; absorbed radiation doses: 5.3 kGy; time zero in the abscissa is the time of initiation of the irradiation; ● : no exposure to air without agitation; ■ : no exposure to air under constant agitation; ◆ : under constant exposure to air with constant agitation; the initial concentration of the palladate ion: 0.2 mM; pH = 1.95 HCl.

HCl, pH=1.95, dose:5.3kGy

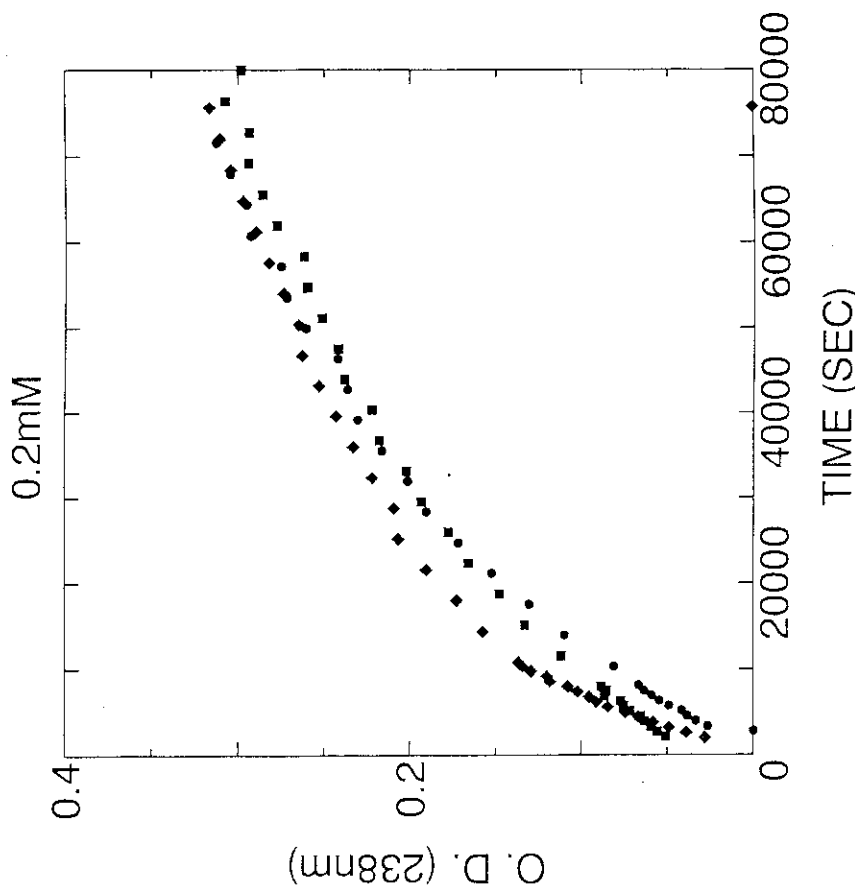


Fig. 7B Absorbance (O.D.) at 238 nm as a function of time for the solutions with or without the presence of oxygen and agitation by a magnetic stirrer; absorbed radiation doses: 5.3 kGy; time zero in the abscissa is the time of initiation of the irradiation; ● : no exposure to air without agitation; ■ : no exposure to air under constant agitation; ◆ : under constant exposure to air with constant agitation; the initial concentration of the palladate ion: 0.2 mM; pH = 1.95 HCl.

HCl, pH=1.95, dose:5.3kGy

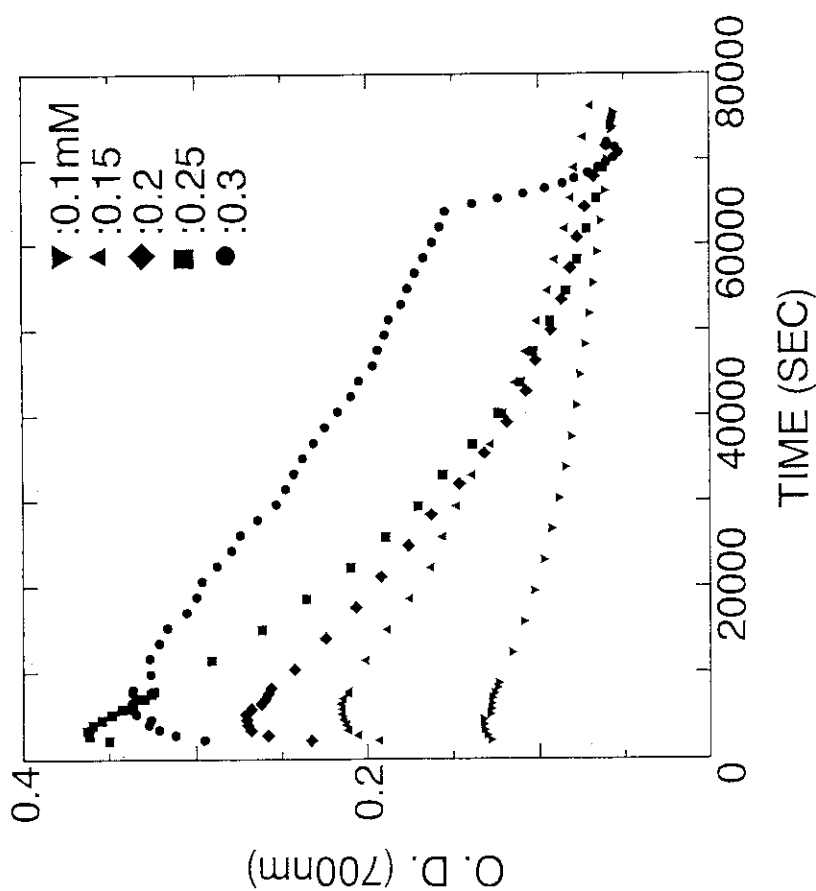


Fig. 8A Absorbance (O. D.) at 700 nm as a function of time for the solutions containing sodium chloro-palladate of different concentrations; time zero in the abscissa is the time of initiation of the irradiation; ● : 0.3 mM; ■ : 0.25 mM; ◆ : 0.2 mM; ▲ : 0.15 mM; ▼ : 0.1 mM; pH = 1.95 with HCl; dose: 5.3 kGy. Agitation initiated at 63 msec resulted discontinuous decrease of O. D. (●).

HCl, pH=1.95, dose:5.3kGy

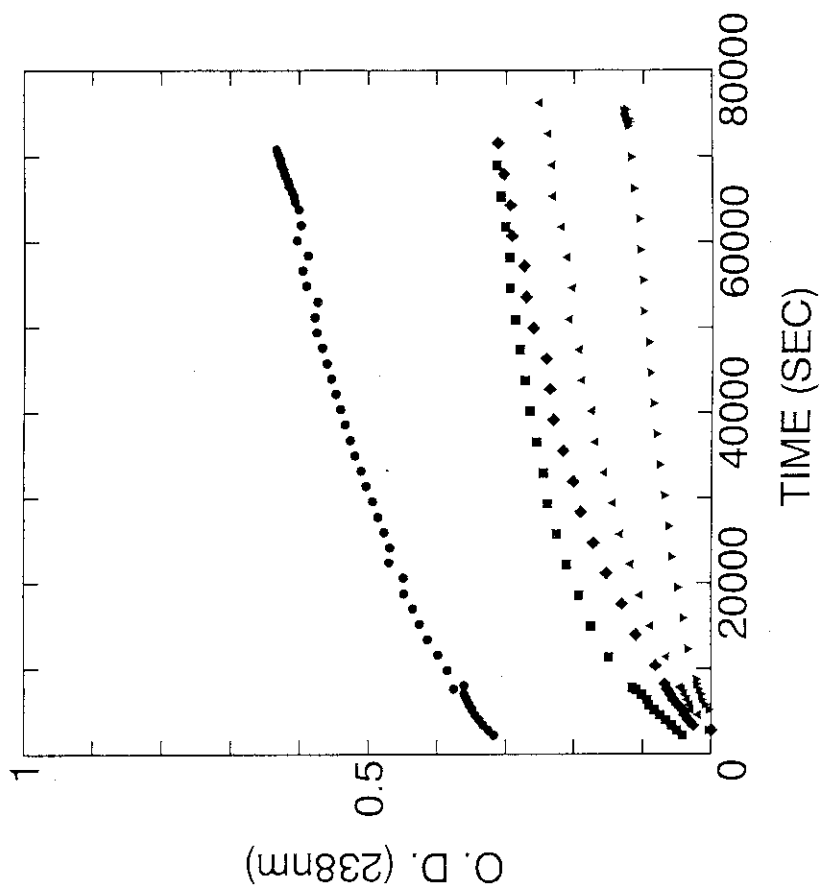


Fig. 8B Absorbance (O. D.) at 238 nm as a function of time for the solutions containing sodium chloro-palladate of different concentrations; time zero in the abscissa is the time of initiation of the irradiation; ● : 0.3 mM; ■ : 0.25 mM; ◆ : 0.2 mM; ▲ : 0.15 mM; ▼ : 0.1 mM; pH = 1.95 with HCl; dose: 5.3 kGy.

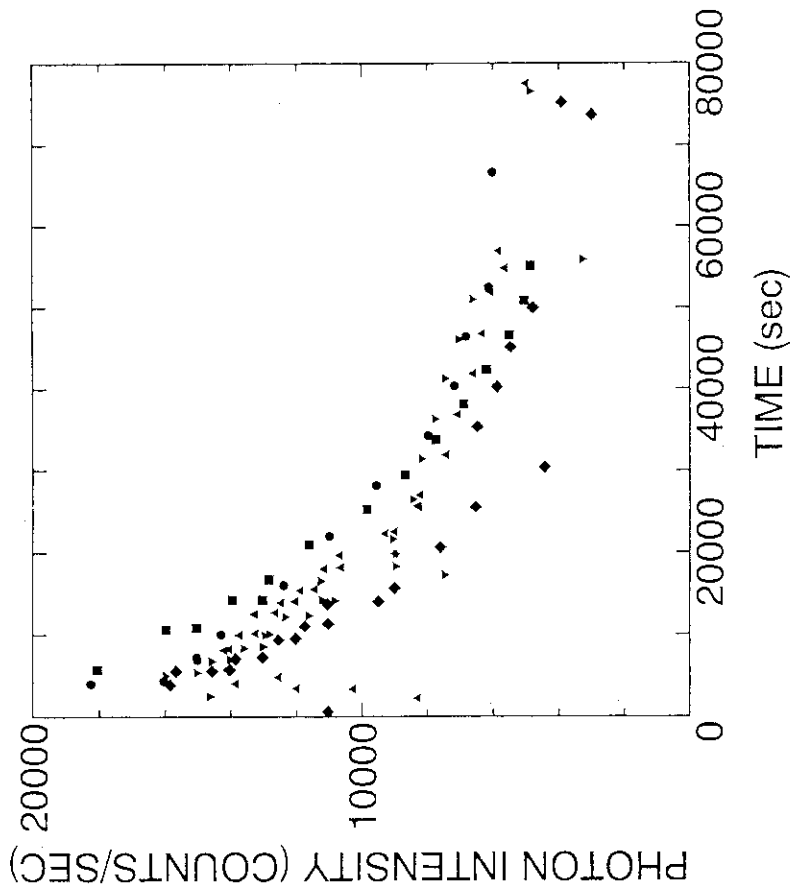


Fig. 8C. Scattering photon intensity as a function of time for the solutions containing sodium chloro-palladate of different concentrations; time zero in the abscissa is the time of initiation of the irradiation; ● : 0.3 mM; ■ : 0.25 mM; ◆ : 0.15 mM; ▲ : 0.2 mM; ▼ : 0.1 mM; pH = 1.95 with HCl; dose: 5.3 kGy.

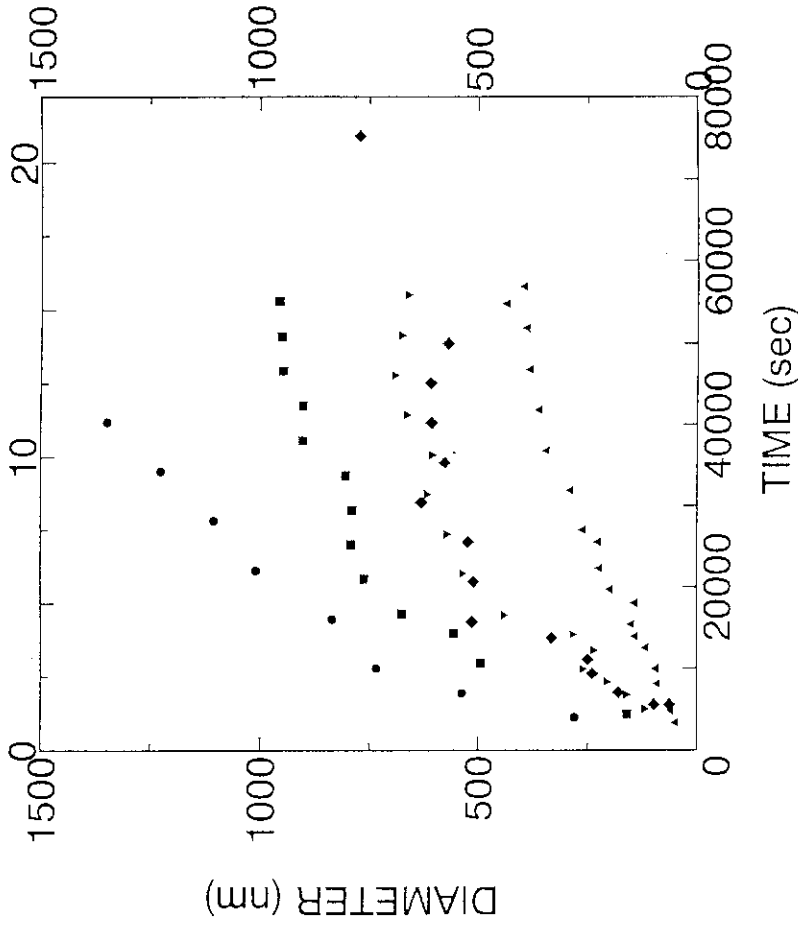


Fig. 8D. Average particle diameter as a function of time for the solutions containing sodium chloro-palladate of different concentrations; time zero in the abscissa is the time of initiation of the irradiation; ● : 0.3 mM; ■ : 0.25 mM; ◆ : 0.15 mM; ▲ : 0.2 mM; ▼ : 0.1 mM; pH = 1.95 with HCl; dose: 5.3 kGy.

pH=1.95 ○ 2.75; □ 3.21; ◇ 5.5; △ 8.25; ▽ 11.0 kGy
 pH=0.65 ◆ 5.3; ▲ 7.95; ▼ 10.6; + 15.

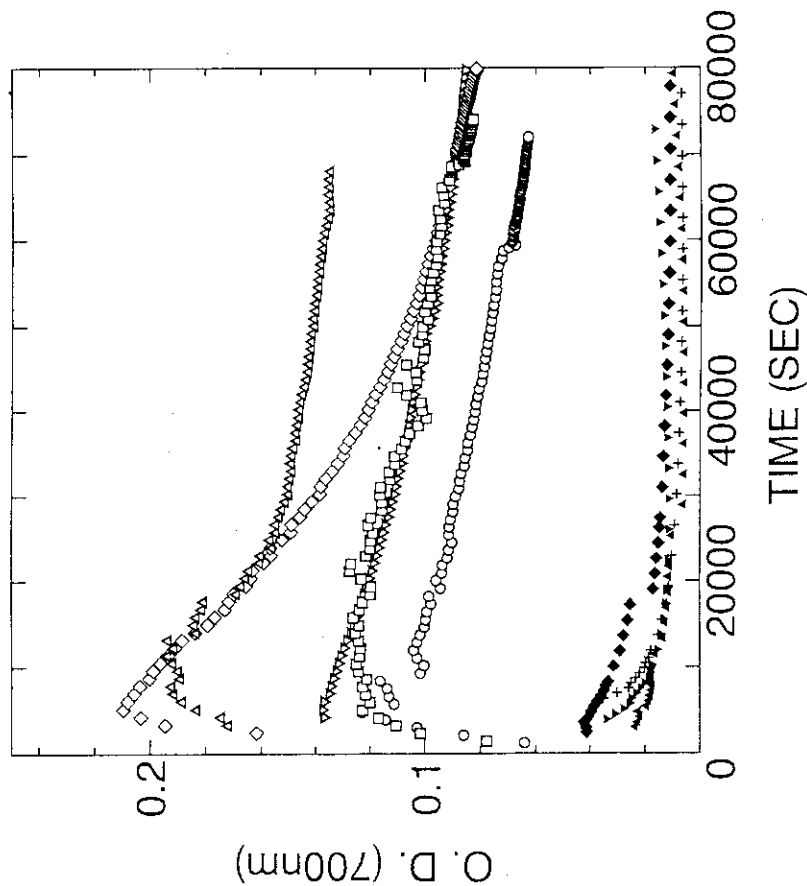


Fig. 10A Absorbance (O. D.) at 700 nm as a function of time for the solutions of different absorbed doses of radiation; time zero in the abscissa is the time of initiation of the irradiation; pH = 0.65 with HCl; concentration of sodium chloro-palladate: 0.3 mM; ◆ : 5.3; ▲ : 7.95; ▼ : 10.6; + : 15.9 kGy; the plots obtained for the solution of pH = 1.95 are also shown for comparison (Fig. 5A).

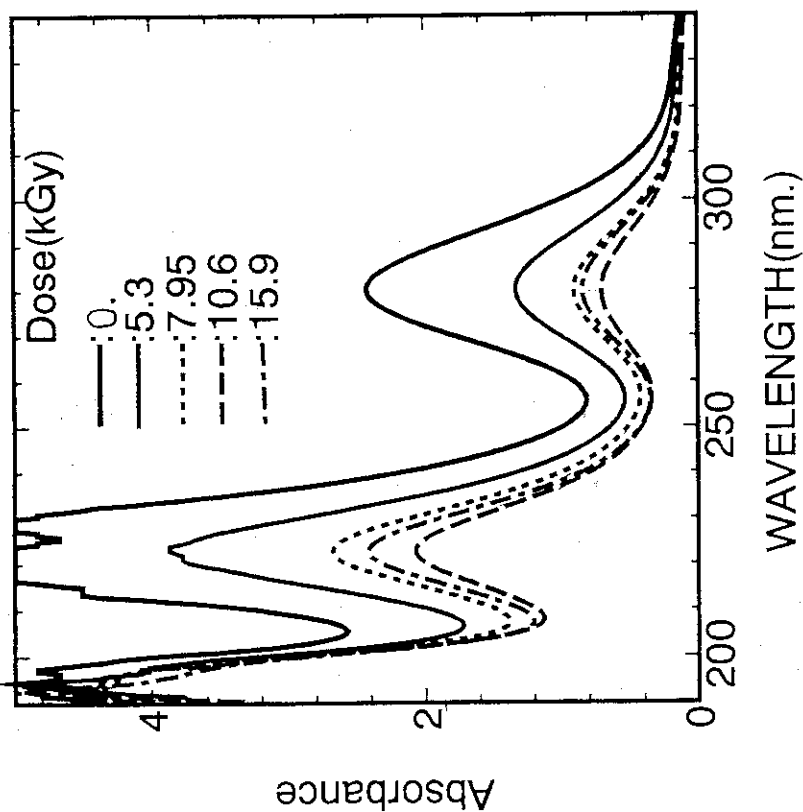


Fig. 9 Electronic spectra of aqueous solution of palladate ions after irradiation of different doses; pH = 0.65, HCl; concentration of sodium chloro-palladate: 0.3 mM.

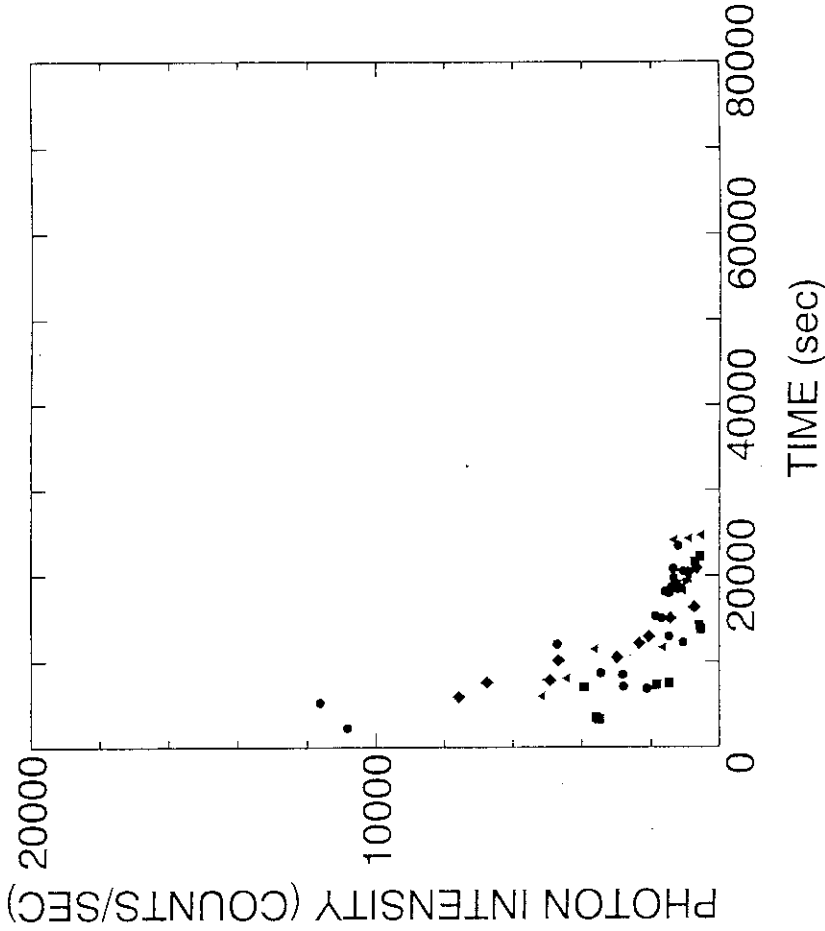


Fig. 10C Scattering photon intensity as a function of time for the solutions of different absorbed doses of radiation; time zero in the abscissa is the time of initiation of the irradiation; pH = 0.65 with HCl; concentration of sodium chloro-palladate: 0.3 mM; ● : 5.3; ■ : 7.95; ◆ : 0.10.6; ▲ : 15.9 kGy.

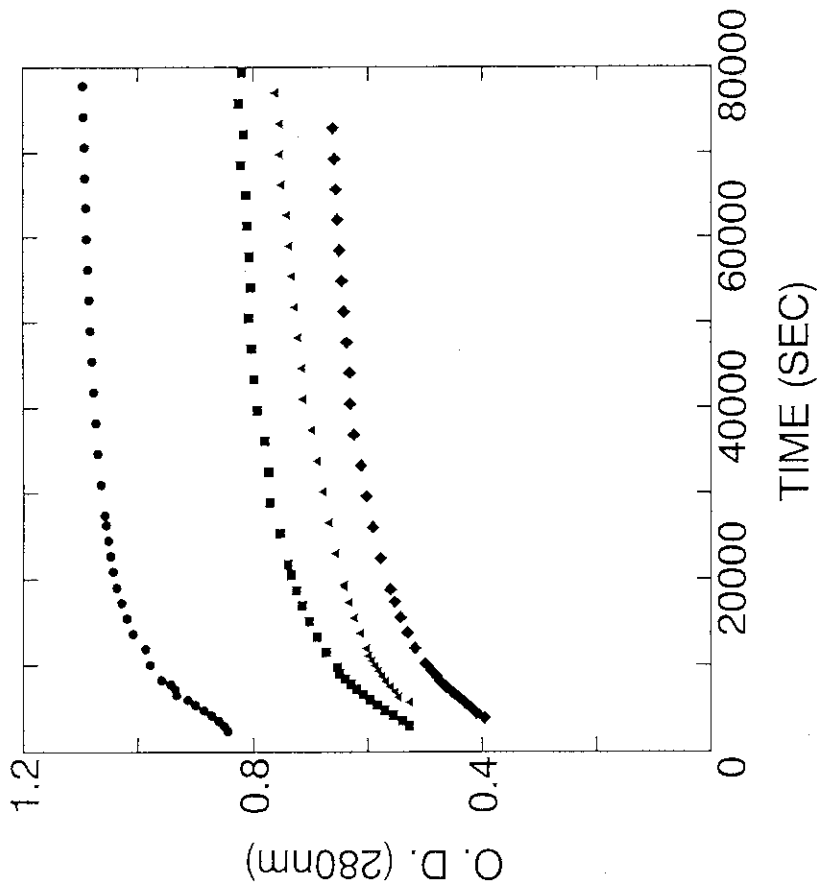


Fig. 10B Absorbance (O. D.) at 280 nm as a function of time for the solutions of different absorbed doses of radiation; time zero in the abscissa is the time of initiation of the irradiation; pH = 0.65 with HCl; concentration of sodium chloro-palladate: 0.3 mM; ● : 5.3; ■ : 7.95; ◆ : 0.10.6; ▲ : 15.9 kGy.

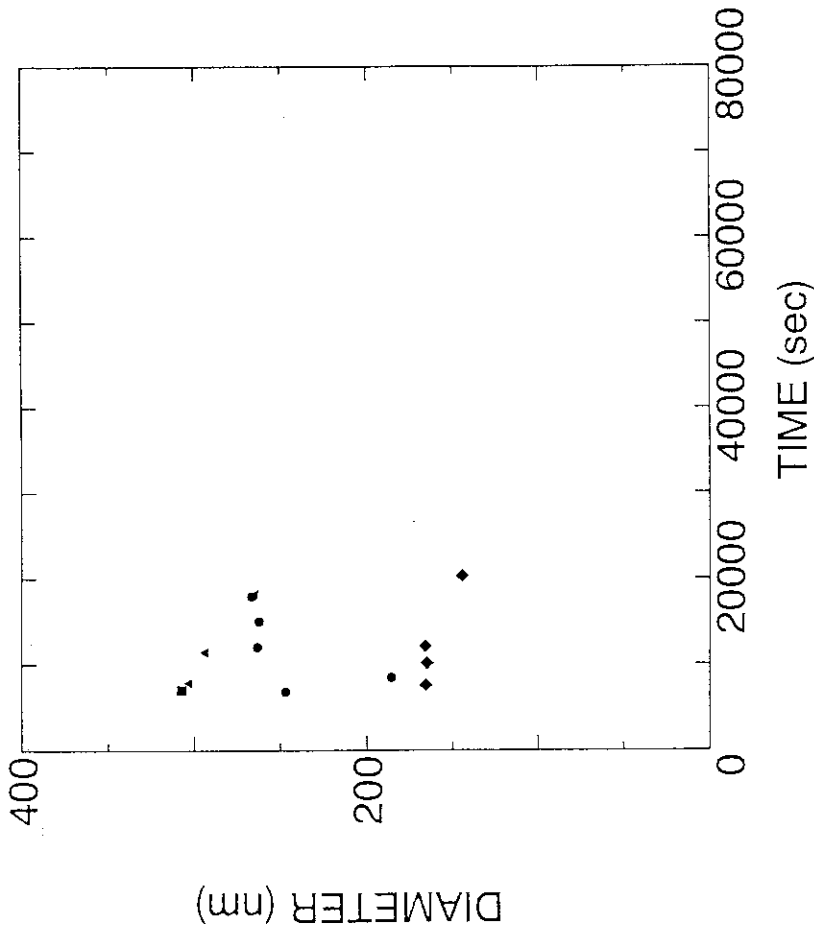


Fig. 10D Average particle diameter as a function of time for the solutions of different absorbed doses of radiation; time zero in the abscissa is the time of initiation of the irradiation; pH = 0.65 with HCl; concentration of sodium chloro-palladate: 0.3 mM; ● : 5.3; ■ : 7.95; ◆ : 0.10.6; ▲ : 15.9 kGy.

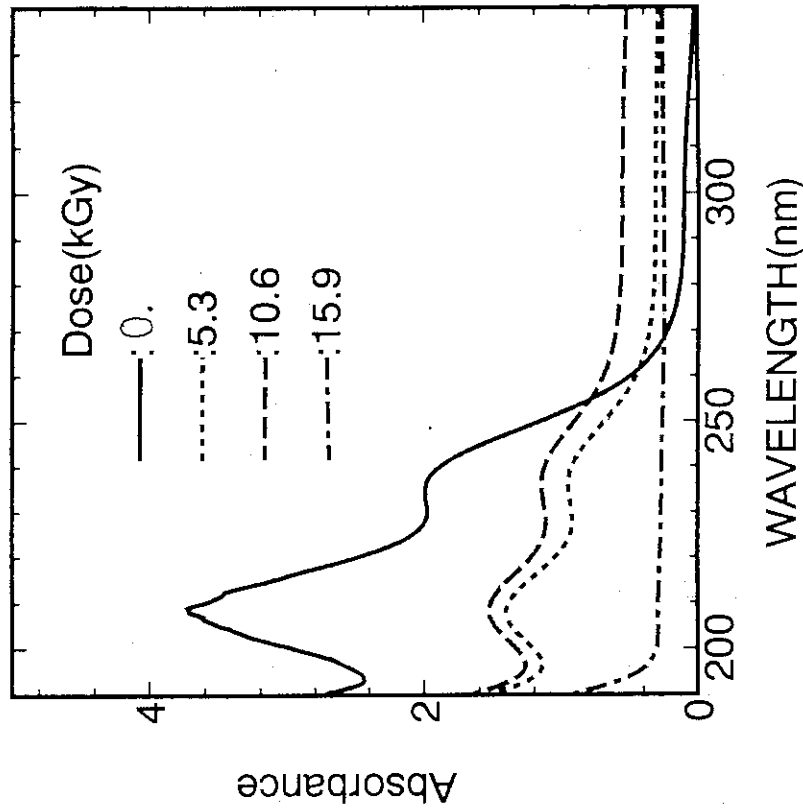


Fig. 11 Electronic spectra of aqueous solution of palladate ions after irradiation of different doses; pH = 1.95, HClO₄; concentration of sodium chloro-palladate: 0.3 mM.

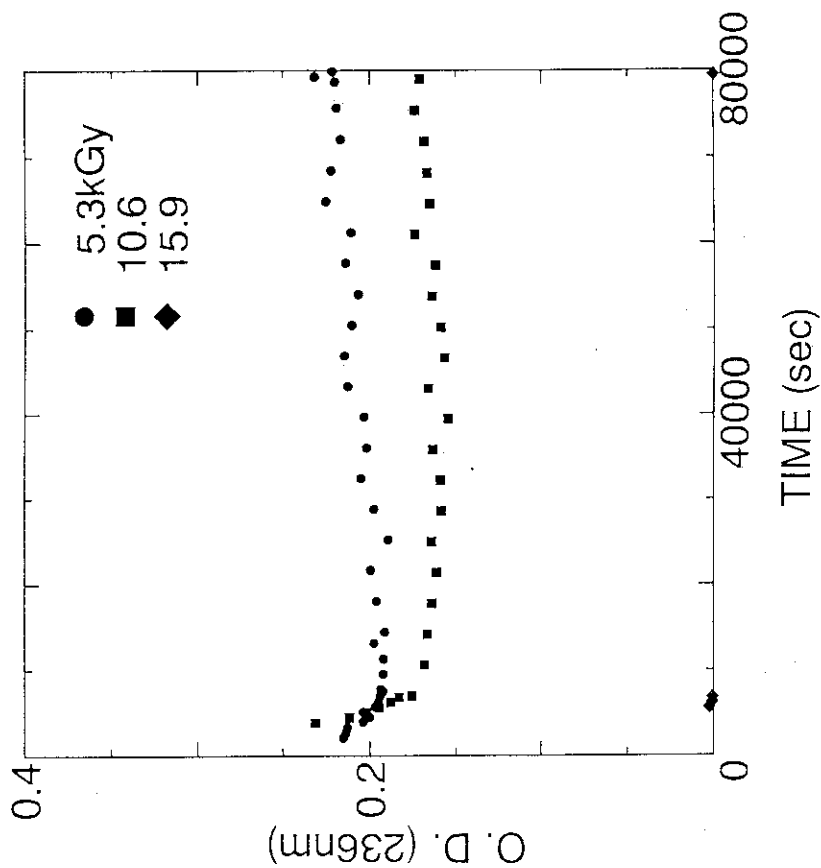


Fig. 12B. Absorbance (O. D.) at 236 nm as a function of time for the solutions of different absorbed doses of radiation; time zero in the abscissa is the time of initiation of the irradiation; pH = 1.95 with HClO₄; concentration of sodium chloro-palladate: 0.3 mM; ● : 5.3; ■ : 10.6; ◆ : 15.9;.

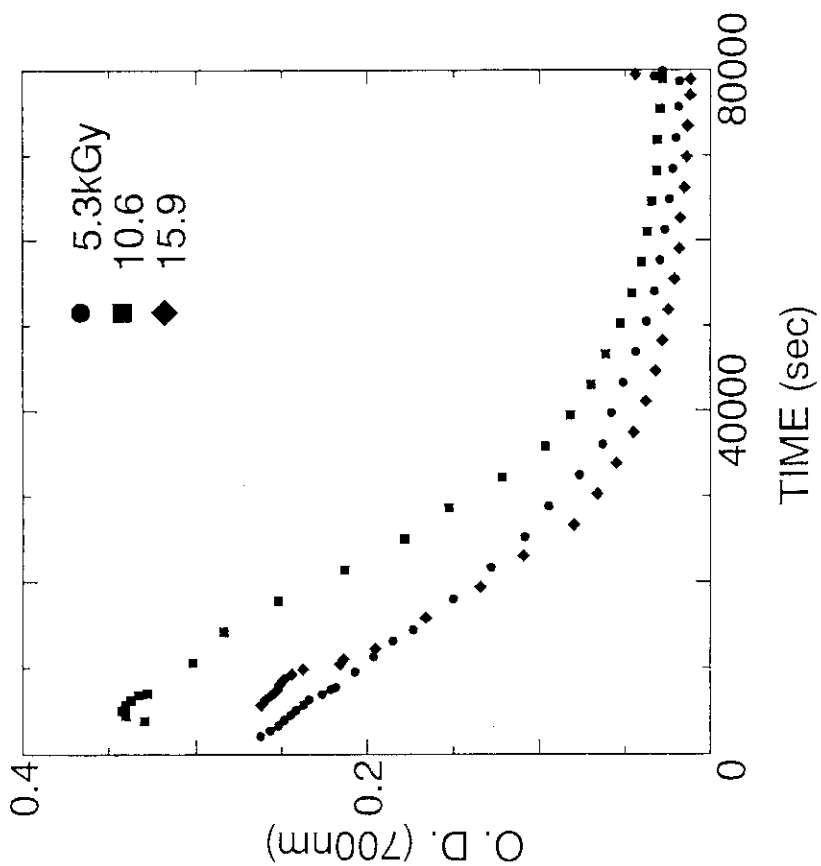


Fig. 12A. Absorbance (O. D.) at 700 nm as a function of time for the solutions of different absorbed doses of radiation; time zero in the abscissa is the time of initiation of the irradiation; pH = 1.95 with HClO₄; concentration of sodium chloro-palladate: 0.3 mM; ● : 5.3; ■ : 10.6; ◆ : 15.9;.

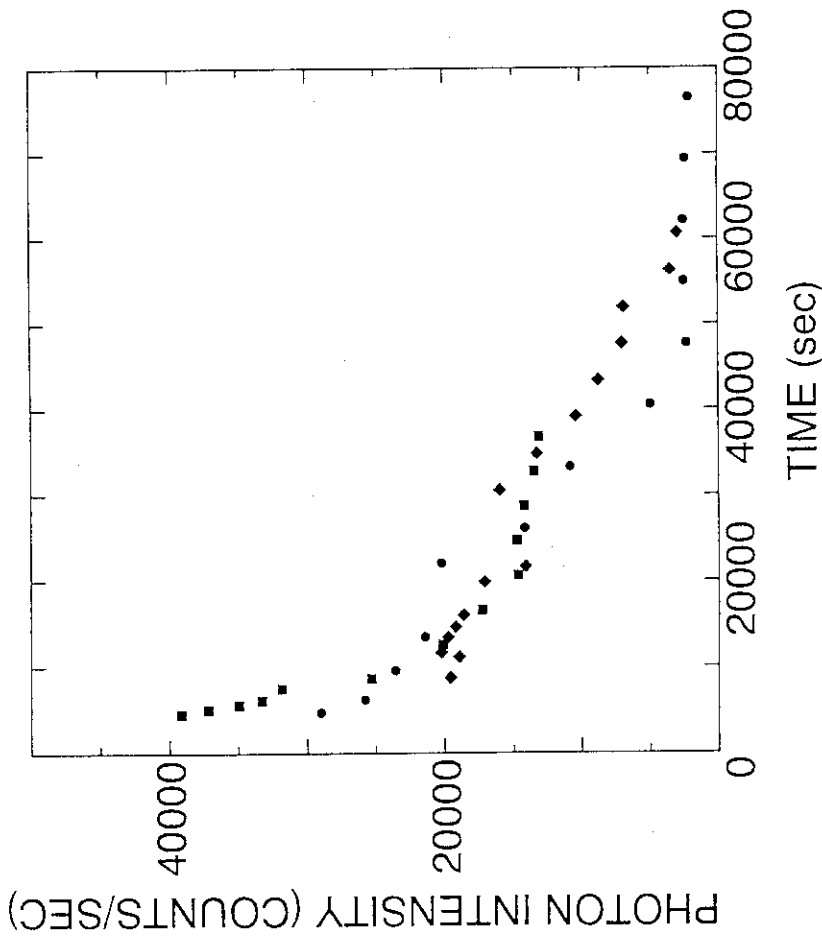


Fig. 12C. Scattering photon intensity as a function of time for the solutions of different absorbed doses of radiation; time zero in the abscissa is the time of initiation of the irradiation; pH = 1.95 with HClO₄; concentration of sodium chloro-palladate: 0.3 mM; ● : 5.3; ■ : 10.6; ◆ : 15.9.

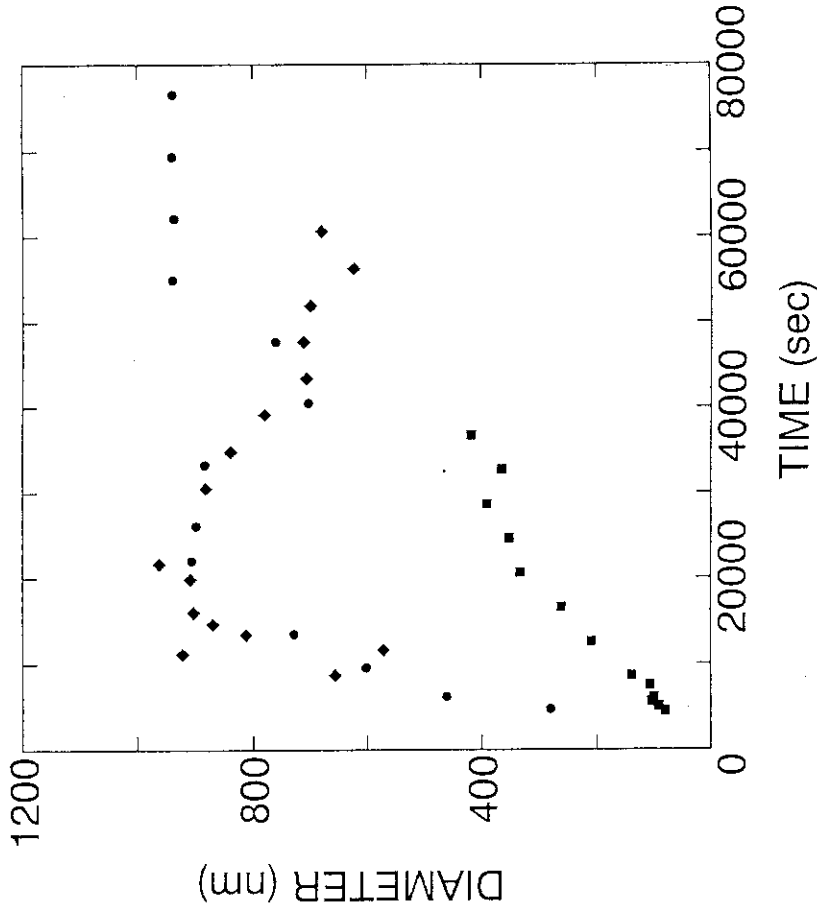


Fig. 12D. Average particle diameter as a function of time for the solutions of different absorbed doses of radiation; time zero in the abscissa is the time of initiation of the irradiation; pH = 1.95 with HClO₄; concentration of sodium chloro-palladate: 0.3 mM; ● : 5.3; ■ : 10.6; ◆ : 15.9.

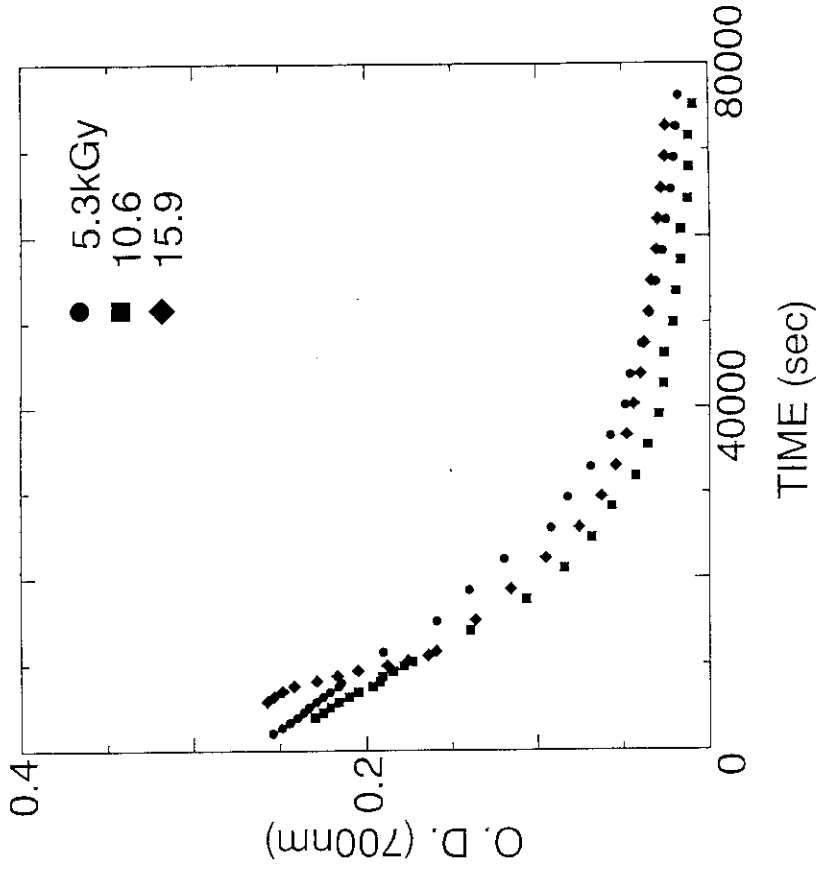


Fig. 14A. Absorbance (O.D.) at 700 nm as a function of time for the solutions of different absorbed doses of radiation; time zero in the abscissa is the time of initiation of the irradiation; pH = 0.65 with HClO₄; concentration of sodium chloro-palladate: 0.3 mM; ● : 5.3; ■ : 10.6; ◆ : 15.9;.

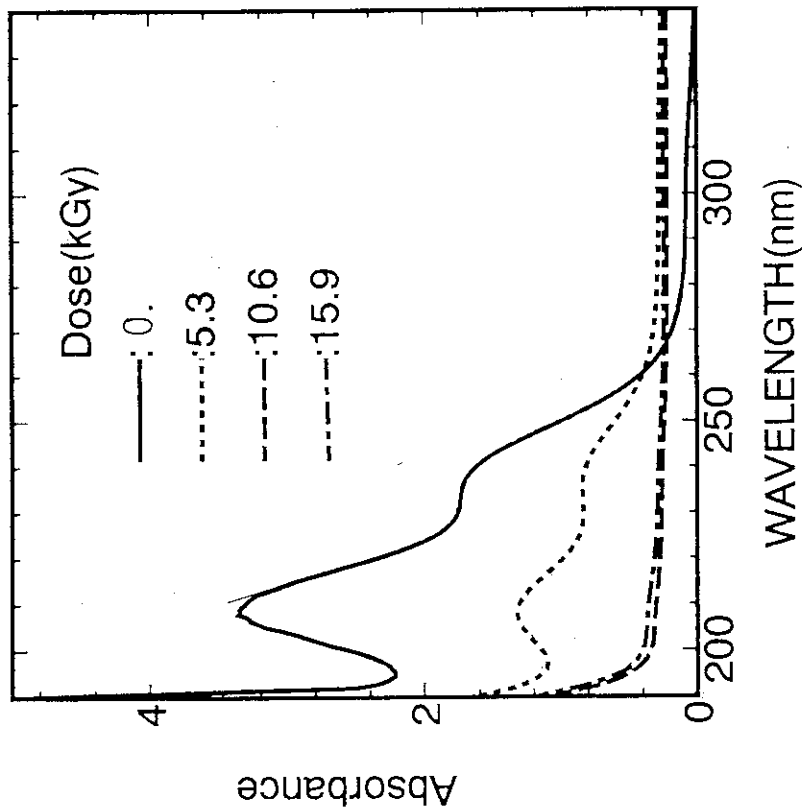


Fig. 13. Electronic spectra of aqueous solution of palladate ions after irradiation of different doses; pH = 0.65, HClO₄; concentration of sodium chloro-palladate: 0.3 mM.

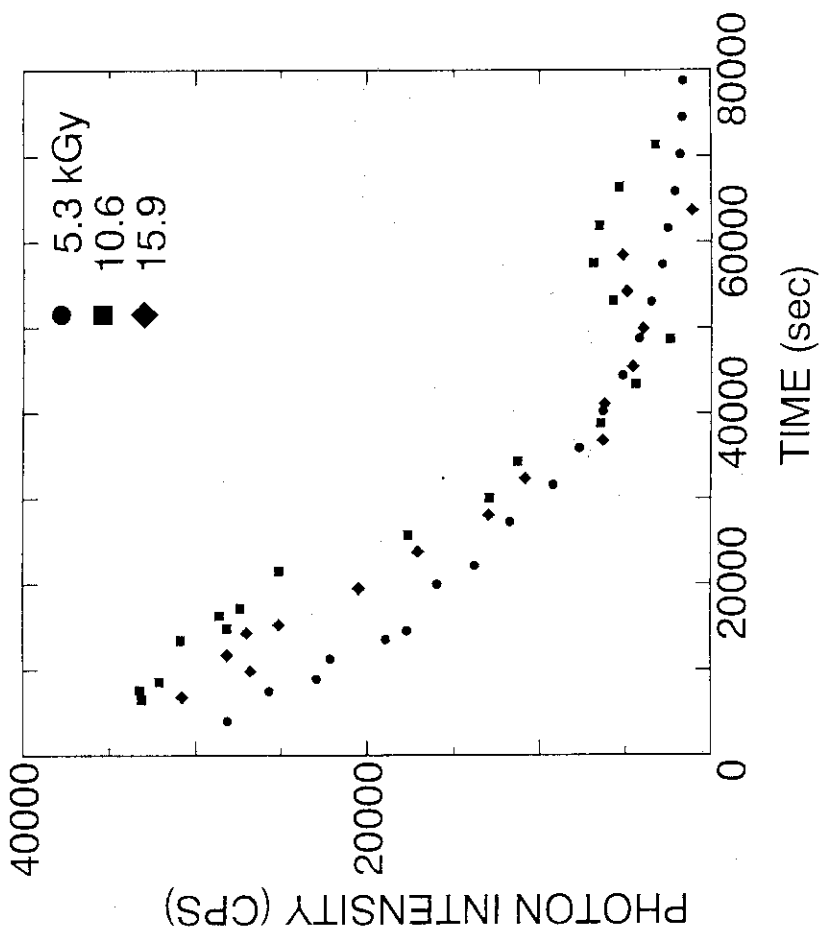


Fig. 14C. Scattering photon intensity as a function of time for the solutions of different absorbed doses of radiation; time zero in the abscissa is the time of initiation of the irradiation; pH = 0.65 with HClO₄; concentration of sodium chloro-palladate: 0.3 mM; ● : 5.3; ■ : 10.6; ◆ : 15.9.

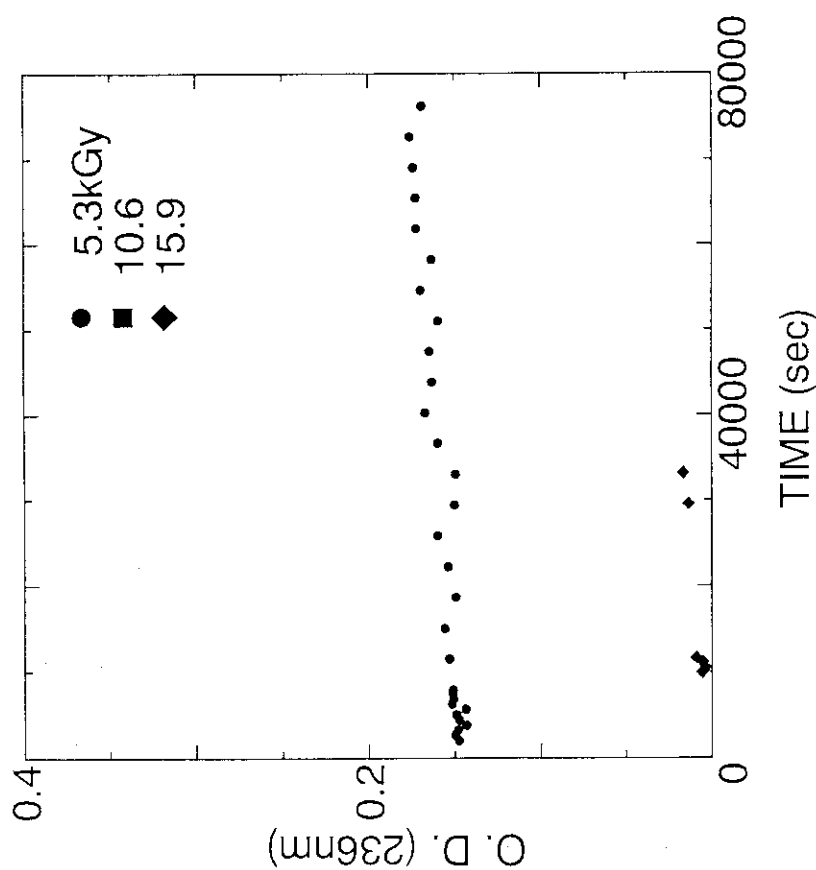


Fig. 14B. Absorbance (O. D.) at 236 nm as a function of time for the solutions of different absorbed doses of radiation; time zero in the abscissa is the time of initiation of the irradiation; pH = 0.65 with HClO₄; concentration of sodium chloro-palladate: 0.3 mM; ● : 5.3; ◆ : 15.9; ■ : 10.6.

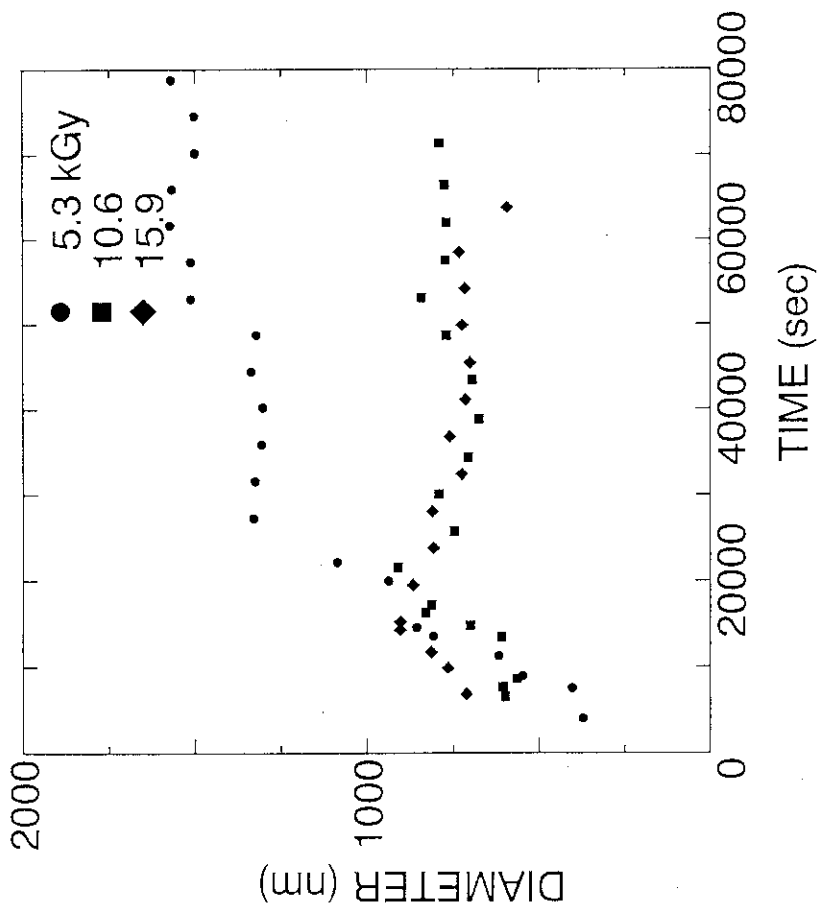


Fig. 14D Average particle diameter as a function of time for the solutions of different absorbed doses of radiation; time zero in the abscissa is the time of initiation of the irradiation; pH = 0.65 with HClO₄; concentration of sodium chloro-palladate: 0.3 mM; ● : 5.3; ■ : 10.6; ◆ : 15.9 kGy.

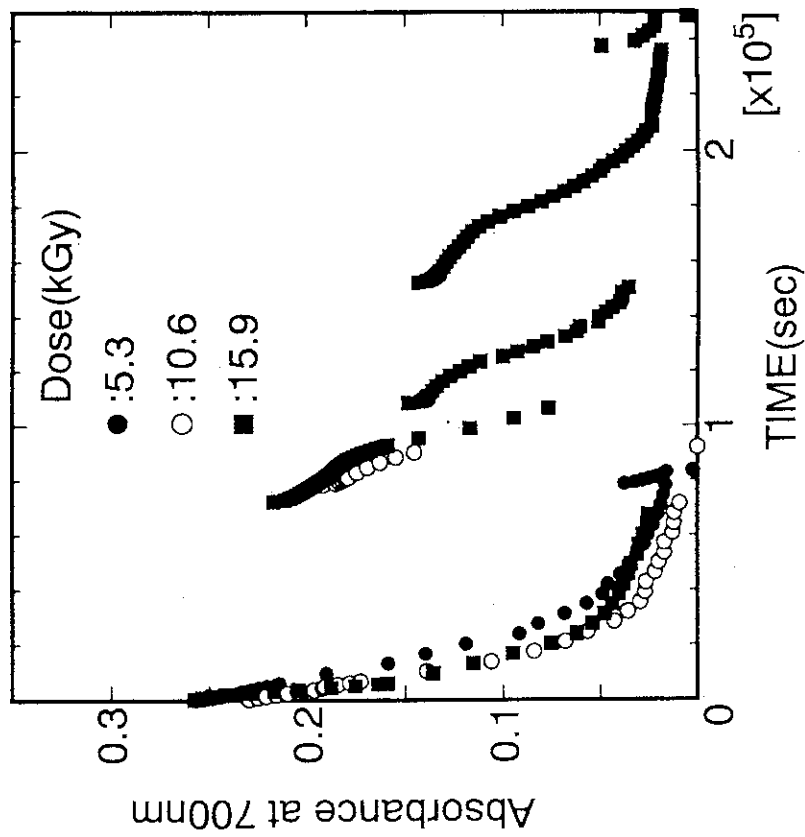


Fig. 15A Absorbance (O.D.) at 700 nm as a function of time; supersonic agitation was made at every time after the particles floating in the solution were settled down; time during the supersonic agitation is not excluded from the time scale in the figure; pH = 0.65 with HClO₄; concentration of sodium chloro-palladate: 0.3 mM; ● : 5.3; ■ : 10.6; ◆ : 15.9 kGy.

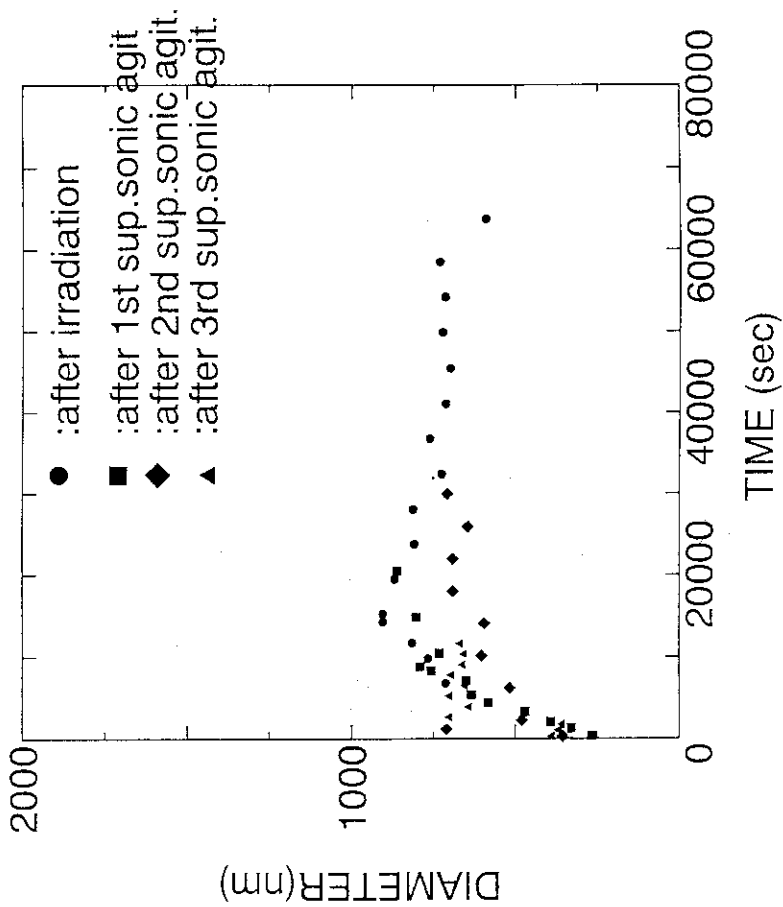


Fig. 15B Scattering photon intensity as a function of time after the irradiation or after the supersonic agitation; the supersonic agitation was made at every time after the particles floating in the solution were settled down; time during the supersonic agitation is not excluded from the time scale in the figure; pH = 0.65 with HClO₄; concentration of sodium chloro-palladate: 0.3 mM; 15.9 kGy.

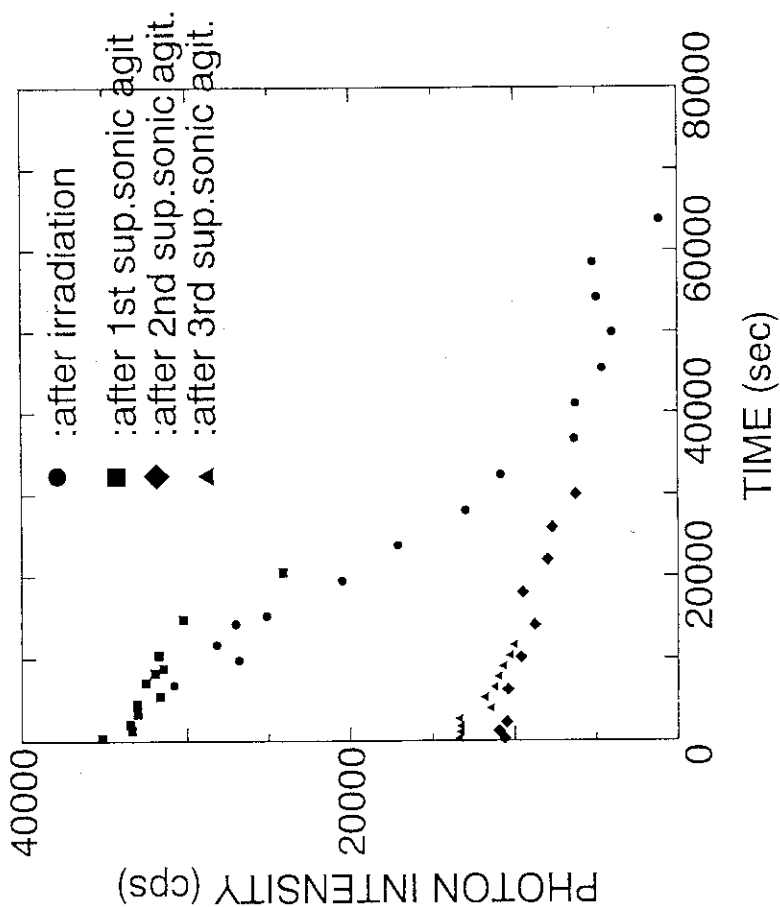


Fig. 15C Average particle diameter as a function of time after the irradiation or after the supersonic agitation; the supersonic agitation was made at every time after the particles floating in the solution were settled down; time during the supersonic agitation is not excluded from the time scale in the figure; pH = 0.65 with HClO₄; concentration of sodium chloro-palladate: 0.3 mM; 15.9 kGy.

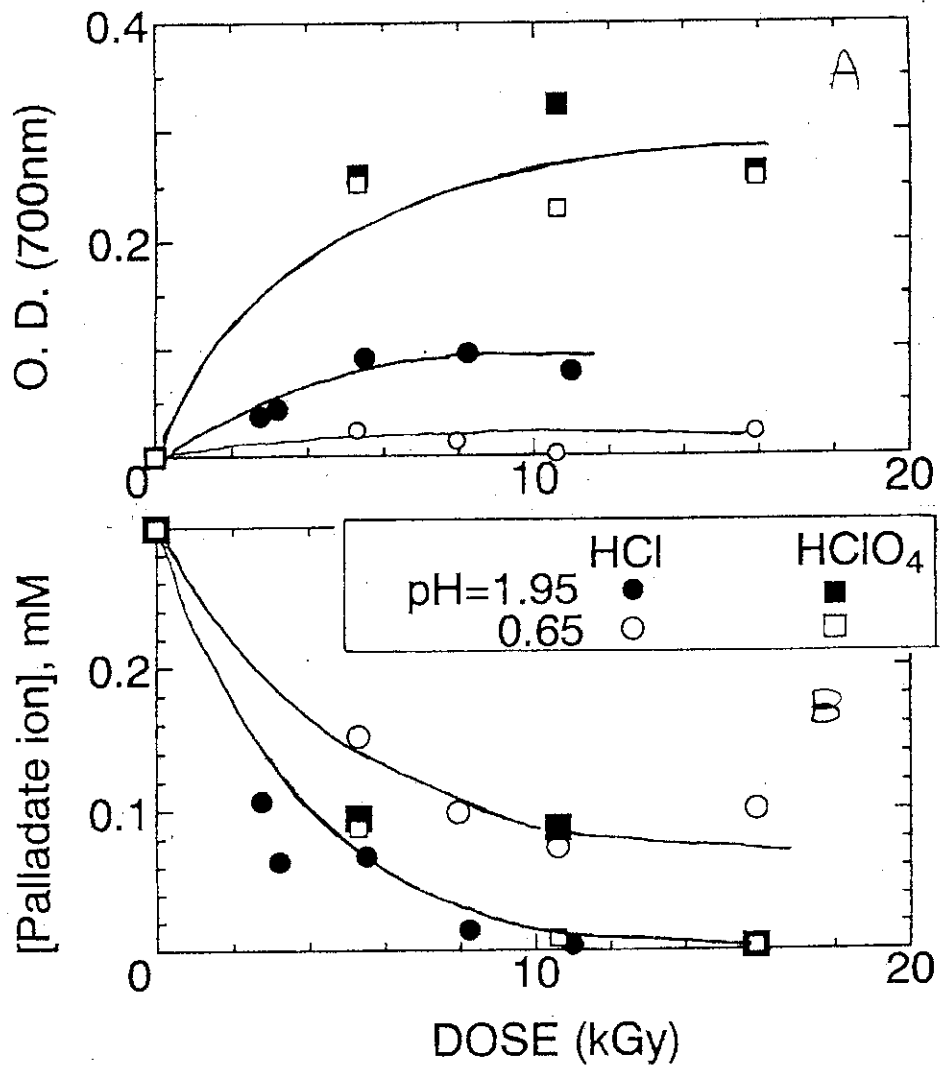


Fig. 16 The amounts of particles produced and the amounts of palladate ions consumed as a function of time for four different solutions of pH's and acids; (A) the turbidity as a function of dose; (B) the concentration of palladate ions as a function of dose.

APPENDIX

The basic program to convert spectral data to O. D.-time data directly from the data files (.SPC) obtained on a Shimadzu UVPC3101 spectrophotometer; the lines until L.980 were taken from the earlier work[2].

```

10 REM THIS CONVERTS UV.SPC DATA TO ASC.FILE; THEN MAKES AVERAGE O.D. FRO
M 680 TO 700nm AND MAKES AVERAGE O.D. AT 236nm PEAK;
12 REM THIS PROCEDURE WAS MADE FOR A SERIES OF SPECTRA TAKEN INTERMITTE
NTLY ONE AFTER ANOTHER, AND COVERT TO O.D.(700nm/236nm) VS TIME PLOT;
14 REM THIS PROGRAM IS USED FOR pH 1.95 BY HCl, 0.65 AND 1.95 BY HClO4 AQ. SO
LUTIONS OF SODIUM CHLOROPALLADATE.
20 DIM WWW(2500),YYY(2500)
30 INPUT "FILE NAME to be written on drive B"; WRTNM$
40 WRTNAM$="B:"+WRTNM$+".DAT"
45 OPEN WRTNAM$ FOR OUTPUT AS #2
50 AS$=".ASC":SP$=".SPC"
60 INPUT "FILE NAME to be read on A drive";OTNAM$
70 INPUT "Enter maximum file number of INPUT FILES";MAXFLNB
180 INPUT "TIME ZERO";TZERO
190 INPUT "TIME STEP";STEPTIME
280 FOR J=0 TO MAXFLNB
300 NUMB$=STR$(J)
310 NC=LEN(NUMB$)
320 NUMB$=RIGHT$(NUMB$,NC-1)
330 IF J<10 THEN NUMB$="0"+NUMB$
340 FILENAME1$="A:"+OTNAM$+NUMB$+SP$
380 GOSUB*CONVASC
400 REM
440 'PRINT 440
450 'END
500 SS(0)=.5
502 WLL=680:WLH=700
510 CC=0:YY(0)=0!:YY(1)=0!:YY(2)=0!
520 YAV=0!
530 COUNT=0
540 LL=0
550 PKSCH=0
560 FOR I=1 TO WWWMAX
565 W=WWW(I):Y=YYY(I)
570 IF PKSCH=1 THEN GOTO 740
580 IF W>WLH THEN GOTO 800
590 IF W<=WLH AND W>=WLL THEN COUNT=COUNT+1:YAV=YAV+Y:GOTO 800
600 IF W>WLL THEN GOTO 800
610 IF COUNT=0 THEN PRINT "NO DATA POINT":CLOSE:STOP
620 IF LL=1 THEN GOTO 640
630 YAV=YAV/COUNT:LL=1
640 'PEAK SEARCH
650 IF W>263 THEN GOTO 800
660 IF W=263 THEN Y263=Y:GOTO 800
665 IF W<263 AND W>245 THEN GOTO 800
670 IF W<245 THEN WP=W:YP=Y:YY(1)=Y:DY=YY(1)-YY(0):YY(0)=YY(1)
680 IF DY<0 THEN CC=CC+1 ELSE CC=0
690 IF CC>1 THEN GOTO 720 ELSE GOTO 800
700 '
710 '
720 PRINT "PEAK is ";WP;" ABS is ";YP
730 PKSCH=1
740 'PEAK EDGE SERARCH *****
745 IF W>211 THEN GOTO 800
750 SLOAP=(Y-Y263)/(263-W):WS=W:YS=Y
760 SS(1)=SLOAP:DS=SS(1)-SS(0):SS(0)=SS(1)
770 IF DS>0 THEN DD=DD+1 ELSE DD=0
780 IF DD>2 THEN GOTO 810 ELSE GOTO 800
790 PRINT "W SHORT is ";WS;"ABS S is ";YS

```



```

800 NEXT I
810 'CALCULATION *****
820 YPCR=(YP+SLOAP*(WP-263)-Y263)
830 TIME=TZERO + J*STEPTIME:PRINT TIME,YAV,WP,YPCR
840 PRINT #2,"
850 PRINT #2,USING "##### ###.### ##.## ##.###";TIME;YAV;WP;YPCR
860 PRINT #2,"

870 CLOSE #1
880 GOTO 910
890 REM DUMMY STATEMENT
900 RESUME 910
910 NEXT J
920 INPUT "IF YOU WISH TO ADD ANOTHER SEQUENCE TO FILE ENTER I";YN
930 IF YN=1 THEN GOTO 60
940 CLOSE #2
950 PRINT:PRINT "Data are saved in file ";OUTNAMES$
960 'PRINT "Wavelength range is ";WL; " to ";VALUE
970 'PRINT DVAL
980 END
1000 *CONVASC:'Convert UV spectrum file (Shimazu in JAERI)
1070 OPEN FILENAME1$ FOR INPUT AS #1
1090 PRINT "Convert "; FILENAME1$; " ==> "; FILENAME2$
1100 '
1110 ' Read Header
1120 W$ = INPUT$(10, #1)
1130 FLOATDATAS$=INPUT$(4, #1): GOSUB *CONV87BASUB: MAXWAVEL=CVS(FLOATDATAS$
)
1140 FLOATDATAS$=INPUT$(4, #1): GOSUB *CONV87BASUB: MINWAVEL=CVS(FLOATDATAS$)
1150 W$ = INPUT$(100, #1)
1160 NDATA = CVI(INPUT$(2, #1))
1170 STEPWAVEL = (MAXWAVEL - MINWAVEL) / (NDATA - 1)
1180 'PRINT "Wavelength = "; MAXWAVEL; " - "; MINWAVEL; " nm"
1190 'PRINT "Number of data points = "; NDATA, "Step = "; STEPWAVEL; " nm"
1200 '
1210 ' Read Data
1220 I=0
1230 WHILE (NOT EOF(1))
1240 WWW(I) = MAXWAVEL - STEPWAVEL * I
1250 FLOATDATAS$=INPUT$(4, #1): GOSUB *CONV87BASUB: YYY(I)=CVS(FLOATDATAS$)
1270 I=I+1:WWWMAX=I
1280 WEND
1290 CLOSE #1
1305 RETURN
1310 END
1320 '
1330 'Convert floating point format
1340 ' IEEE (8087) format ==> BASIC format
1350 ' Input and Output : FLOATDATAS$ (length=4)
1360 ' FLOATDATAS$ : Low-Mid-High-Exp
1370 *CONV87BASUB
1380 DATAEXP=ASC(MID$(FLOATDATAS$,4,1))
1390 DATAHIGH=ASC(MID$(FLOATDATAS$,3,1))
1400 DATAMID=ASC(MID$(FLOATDATAS$,2,1))
1410 DATALOW=ASC(MID$(FLOATDATAS$,1,1))
1420 DATAEXP2=(DATAEXP AND 127)*2 + (DATAHIGH AND 128)¥128
1430 DATAHIGH2=(DATAEXP AND 128) + (DATAHIGH AND 127)
1440 IF DATAEXP2=0 THEN DATAEXP2=0: DATAHIGH2=0: DATAMID=0: DATALOW=0: GOTO
*CV8END: ' Zero or Underflow
1450 DATAEXP2=DATAEXP2+2
1460 IF DATAEXP2>=256 THEN DATAEXP2=255: DATAHIGH2=(DATAHIGH2 OR 127): DATAM
ID=255: DATALOW=255: GOTO *CV8END: ' Overflow
1470 *CV8END
1480 FLOATDATAS$=CHR$(DATALOW)+CHR$(DATAMID)+CHR$(DATAHIGH2)+CHR$(DATAEXP2)
1490 RETURN

```