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# GROWTH AND SEDIMENTATION OF FINE PARTICLES PRODUCED IN AQUEOUS SOLUTIONS OF PALLADIUM SULFATE AND PALLADIUM SULFATE-SILVER SULFATE INDUCED BY GAMMA-RAY IRRADIATION

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Motoyoshi HATADA and Charles D. JONAH*

日本原子力研究所
Japan Atomic Energy Research Institute

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# Growth and Sedimentation of Fine Particles Produced in Aqueous Solutions of Palladium Sulfate and Palladium Sulfate-silver Sulfate Induced by Gamma-ray Irradiation

Motoyoshi HATADA and Charles D. JONAH*

Osaka Laboratory for Radiation Chemistry
Takasaki Radiation Chemistry Research Establishment
Japan Atomic Energy Research Institute
Mii-minami-machi, Neyagawa-shi, Osaka-fu

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It is known that palladium and palladium-silver fine particles were formed from deaerated aqueous solutions of palladium sulfate and palladium sulfate-silver sulfate induced by gamma-ray irradiation. Changes in particle size and with amount of particles in the solution with time during and after irradiation were studied using dynamic light scattering technique and UV spectrophotometer.

The particles formed from palladium sulfate solution are found to be water-filled bulky particles of diameter of 200 nm, which grow by mutual coagulation even after irradiation was terminated. Average density depends on concentration of palladium ion in the solution and dose, and the lowest density was about 2 g/cm$^3$ for particles of 200 nm obtained from 0.06 mM solution by 2.4 kGy irradiation. The average density of the particles obtained from palladium sulfate-silver sulfate solutions was smaller than those obtained for the corresponding palladium sulfate solutions. Supersonic agitation destroyed coagulated precipitates to form fine particles, but did not form clusters of a few atoms.

Keywords: Palladium, Silver, Fine Particles, Light Scattering, $\gamma$-ray

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* JAERI Foreign Researcher

# 硫酸パラジウム水溶液および硫酸パラジウム－硫酸銀水溶液のγ線照射により生成した金属微粒子の成長と沈降

日本原子力研究所高崎研究所大阪支所
畑田　元義・Charles D. JONAH*

（1994年9月2日受理）

酸素を除いた硫酸パラジウム水溶液或いは硫酸パラジウム－硫酸銀水溶液にγ線を照射すると微粒子金属が生成する。この照射により水溶液中に生成した微粒子の粒子径の時間的変化を動的光散乱装置を用いて測定した。また，可視紫外分光光度計を用いて照射後の水溶液の濁度の時間的変化を測定することにより，溶液中の微粒子の量の変化を調べた。これらのデータから，微粒子の密度，粒子径などのパラメータを求めた。硫酸パラジウム水溶液では，粒子径は照射後も時間とともに増加した。約20,000秒以後では，線量が小さい時には，時間に対して一定の値を示したが，線量が大きいときには，粒子径は時間とともに減少した。この減少は粒子径の大きい粒子が沈降し，小さい粒子径のものが溶液中に残るためであると考えられる。照射により生成し，成長した粒子は，空隙に水分子を多く含んだ低密度のものであると推定される。平均粒子径や密度は線量や水溶液のパラジウムイオン濃度に依存するが，これまでに得られた最低の密度のものは，2.4 kGyの照射で，0.06 mMの溶液について得られたもので約2グラム／cm³であった。硫酸パラジウム－硫酸銀水溶液から得られた粒子は，同じ条件で硫酸パラジウム水溶液から得られた粒子に比べて，密度の小さいものであった。一旦，凝集して出来た沈澱は超音波を照射することにより分散させることはできたが，数原子からなるクラスターにまで分散させることは出来なかった。

高崎研究所（大阪支所）：〒572　大阪府寝屋川市三井南町25－1
＊外国人研究者

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## 1. INTRODUCTION

Extensive studies have been carried out on the formation of fine metallic particles by irradiation of steady beam of gamma rays or pulsed electron beam, and knowledge on character or detailed rechanism of the formation of these fine particles have been accumulated [1]. Most of these studies were carried out on aqueous solutions of metallic ions containing stabilizers. Since the organic stabilizers present in the solutions may cover the surface of metal clusters or aggregates and stabilize these particles, but simultaneously, they may inactiveate the surface of the metal particles when the particles are used as a catalyst, we selected the solutions without the stabilizers and studied the formation of fine particles by gamma-ray irradiation and their growth in the solution, and we reported that palladium particles and palladium-silver particles were formed by gamma ray irradiation of deareated aqueous solutions of palladium sulfate and palladium sulfate-silver sulfate without the presence of surfactants to stabilize the particles, respectively,[2] and showed that the particle size distribution and growth of the particles can possibly be studied by decrease of turbidity and dynamic light scattering[3]. In this paper, we report that change of particle size in the solution with time during irradiation and after irradiation as studied by dynamic light scattering, and that the decay of the turbidity with time can be explained by growth of the particles and sedimentation of the growing particles.

Mechanism of growth of palladium particles in the aqueous solution is of interest in view of the preparation of catalytic functional fine particles from aqueous solution by radiation chemical method, since the knowledge of the mechanism of formation and growth may hopefully open to the way for effective methods to prepare fine particles of desired particle size distribution. The present study has been carried out in order to know the growth of particle size during and after irradiation.

## 2. EXPERIMENTAL

### 2.1 Preparation of the solutions and gamma ray irradiation

## 1. INTRODUCTION

Extensive studies have been carried out on the formation of fine metallic particles by irradiation of steady beam of gamma rays or pulsed electron beam, and knowledge on character or detailed rechanism of the formation of these fine particles have been accumulated [1]. Most of these studies were carried out on aqueous solutions of metallic ions containing stabilizers. Since the organic stabilizers present in the solutions may cover the surface of metal clusters or aggregates and stabilize these particles, but simultaneously, they may inactiveate the surface of the metal particles when the particles are used as a catalyst, we selected the solutions without the stabilizers and studied the formation of fine particles by gamma-ray irradiation and their growth in the solution, and we reported that palladium particles and palladium-silver particles were formed by gamma ray irradiation of deareated aqueous solutions of palladium sulfate and palladium sulfate-silver sulfate without the presence of surfactants to stabilize the particles, respectively,[2] and showed that the particle size distribution and growth of the particles can possibly be studied by decrease of turbidity and dynamic light scattering[3]. In this paper, we report that change of particle size in the solution with time during irradiation and after irradiation as studied by dynamic light scattering, and that the decay of the turbidity with time can be explained by growth of the particles and sedimentation of the growing particles.

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## 2. EXPERIMENTAL

### 2.1 Preparation of the solutions and gamma ray irradiation

Deareated solution of palladium sulfate (1mM) was irradiated by gamma rays and within 3 minutes after irradiation, the solutions were transferred to a cuvette for UV measurement and to a quartz tubing for dynamic light scattering in nitrogen atmosphere as described [3]. The method of UV measurement and DLS particle size measurement were also described [2,3].

Reagent grade methyl viologen was supplied by Nakarai Tesque Co.

Method of preparation of the samples and method of irradiation were described in details in the earlier reports [2,3]. The pH's of the solution were adjusted to 0.43 with sulfuric acid as in the previous experiments.

## 2.2 Turbidity measurements and analysis

Turbidity was determined from absorbance averaged from 680 through 700nm wavelength range where no absorption due to the electronic transitions of related ionic species is observed [3]. In this paper, turbidity is expressed by O. D. at 700nm. Description in this section is only for qualitative understanding of turbidity-time curves appearing in this paper, and not for quantitative simulation of the turbidity-time curves.

Turbidity decrease with time reflects two combined processes of (1) the increase of particle diameter by the growth of the particles and (2) sedimentation of the particles by Stokes law. Here, for simplicity, we consider only the second process of particles having certain size distribution which can be determined by dynamic light scattering (DLS) analysis, and we leave the first process as a matter of consideration at later studies.

Suppose, particles of a uniform radius, r, be distributed uniformly in a UV cuvette. These particles move downward at a velocity given by Stokes law:

$$u = [\ 2 \cdot 980 \cdot (\ \rho - 1.0\ ) \cdot r^2\ ]/(9\ \eta) \qquad [\mathrm{cm/sec}]$$

where u is sedimentation velocity in cm/s, $\rho$ number average density of the particles in g/cm$^3$, and $\eta$ is viscosity of the liquid. The turbidity due to the particles of a radius r (cm) is constant at time $t_1$ which is time required for the top level of the particle zone to reach the top of the light beam and is determined by equation (1):

$$t_1 = L_a / u \qquad [\mathrm{sec}] \quad (1)$$

where $L_a$ (=2.3 cm) is the distance from top of the solution level in the cell to the upper end of the light beam as shown in Fig. 1A. After $t_1$, the turbidity linearly decreases with time as the upper level of the particle zone moves down the beam area until time $t_2$ which is calculated by equation (2):

$$t_2 = L_b / u + t_1 \quad (2)$$

where $L_b$ (=1.3 cm) is the distance from upper end of light beam to the lower end of the beam. Turbidity due to particles of radius r, T(r), is given by the following equations as a function of time:

$$T(r) = T_0(r) \qquad 0 < t < t_1 \quad (3a)$$

$$T(r,t) = T_0(r) [\ 1 - (t-t_1)/(t_2 - t_1)\ ] \qquad t_1 < t < t_2 \quad (3b)$$

Where $T_0(r)$ is the initial value of T(r) at time 0, and given by the following equation,

$$T_0(r) = 1 - n \pi r^2 \quad (4)$$

The n is number of particles of r in 1 $cm^3$ solution. Therefore, T due to the whole particles having distribution function f(r) can be calculated by:

$$T(t) = \int_0^\infty T(r,t)\, f(r)\, dr \quad (5)$$

An example of such a calculation is shown in Fig. 1B using f(r) that was obtained by DLS measurement for aqueous solution of 1 mM palladium sulfate irradiated with 1 kGy by the method described in the later section.

## 2.3 DLS measurements and analysis

DLS measurements were carried out on an OHTSUKA Electronics Inc. DLS 700 photon correlation spectrometer equipped with a He-Ne laser at 90 degree diffraction angle. The number of accumulations was set at 100 and 0.2 mm aperture was normally used. The noise cut filter was not used. All other parameters for measurement were default values.

For analysis of the data, two types of calculations were carried out using programs supplied by the manufacturer: one, UNIMA which assumes unimodal distribution function for particle sizes, and the other, AUTO2 which assumes multi-peak distribution of particle sizes and makes fittings of autocorrelation function using Marquardt method. Some data were further analyzed using other two programs, UMIMM and MAN2 which correspond to the two programs and perform calculation for better fittings by adjusting particle size range (UNIMM and MAN2) and resolution factor of computation (lambda value) (MAN2). However,

most discussions in this study are made on the basis of UMIMA data.

## 2.4 Calculation of average density, number of particles in solution, number of palladium atoms in a particle, and other parameters which describe particles

To obtain a rough picture of the particles, a simple calculation was made in the following. Assuming that the floating particles in an optical path of a cuvette resulted the observed turbidity without overlapping of the particle in the optical path, eq (6) is obtained.

$$I/I_0 = 10^{-OD700} = (1 - n\ell\pi r^2) = 1 - n\pi r^2 \qquad (6)$$

where $I_0$ and I are the intensities of light before and after passing through the solution, respectively; OD700 is optical density at 700nm, $\ell$ is optical path length, r is average diameter of particle, and n is number of particles in 1 ml solution. Since visual examination of the solution immediately after irradiation indicated no precipitation of solid at the bottom of the irradiation vessel, it is further assumed that mass of all ions consumed in the solution is equal to the mass of the particles. This leads to the following equation :

$$\{\Delta OD389/\varepsilon 389\} \times \{A/1000\} = 4/3 \cdot \pi r^3 n d \qquad (7)$$

$$m\,[Pd^{2+}] = \Delta OD389/\varepsilon 389 = Pd_m \quad [mol/l] \qquad (8)$$

where A is the atomic number of palladium (=106.42), d is average density of the particles, $\Delta$OD389 is the decrease of optical density at 389nm by irradiation, and $\varepsilon$389 is molar extinction coefficient of $[Pd(H_2O)]^{2+}$ at 389nm. Combination of these equations resulted in the following equations:

$$d = \frac{\{\Delta OD389/\varepsilon 389\} \times \{106.42/1000\}}{4/3 \cdot \pi r (1 - 10^{-OD700})} \qquad (9)$$

$$n = (1 - 10^{-OD700})/\pi r^2 \qquad (10)$$

$$N_{Pd} = \frac{\{\Delta OD389/\varepsilon 389\} \times N_A}{n \times 1000} \qquad (11)$$

where $N_{Pd}$ and $N_A$ are the number of palladium atoms in a particle and Avogadro number, respectively. It is further necessary to calculate density of the particle in aqueous solution, where palladium atoms are weakly bound by water molecules to form the particle. We assume that the cavities between the palladium atoms in the particle are filled by water molecules with the fill factor of $\alpha$ = 0.74 for f. c. c. packing.

The density of a particle in the aqueous solution, $d_w$, is calculated by the following equation:

$$d_w = [(N_{Pd}/N_A \times 106.42) + (N_W \times 18)] / [4\pi r^3/3] \quad (12)$$

and

$$N_W = [ (r/r_{Pd})^3 \times \alpha - N_{Pd} ] \{ r_{Pd} / r_w \}^3 \quad (12a)$$

where $N_W$ is number of water molecules in a particle, $r_{Pd}$ = 0.138nm is atomic radius of palladium, and $r_w$ = 0.193 nm is molecular diameter of water molecule (see foot note for details).

## 2.5 Supersonic agitation

In one experiment, after most of the particles precipitated, supersonic irradiation of the solution was carried out in order to know whether the particles, or clusters that coagulated are dispersed again to bring back the solution to the state just after the irradiation. The supersonic agitation was repeatedly carried out for one hour after every precipitation in water using a Bransonic model 1200 (output 30W, 45kHz) for one hour. In the other two experiments, the irradiated solution was subjected to the supersonic agitation immediately after the irradiation for two hours , or the un-irradiated solution was subjected to 25 hour super-sonic agitation for reference.

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Radius R of a particle which contains $n_{Pd}$ palladium atoms whose radius is $r_{Pd}$ can be given by:

$$R^3 = (n_{Pd}/\alpha) r_{Pd}^3 \quad (a)$$

where $\alpha$ is a fill factor, and for f. c. c, it is 0.74. The result of tentative calculation indicates that this value is smaller than 0.74 and that in some cases the density of a particle is even less than 1. This does not fit to the case, since we did not observe that there were particles floating on the surface of the solution (d<1.0) (however, in some cases, we observed a weak interference color on the surface). In order to fit the d- values to the observation, it is necessary to consider that the cavities between palladium atoms in the particle are filled with water molecules.

If $n_w'$ molecules and $n_{Pd}$ palladium atoms make a particle of diameter of R with fill factor of $\alpha$, eq (a) becomes:

$$R^3 = (n_w' + n_{Pd}/\alpha) r_a^3 \quad (b)$$

where $r_a = (r_{Pd} + r_w)/2$. From eq (b):

$$n_w' = (R/r_a)^3 \quad \alpha - n_{Pd}$$

Since molecular volume is $\{ r_{Pd} / r_w \}^3 = (1.93/1.38)^3 = 2.7$ times larger than $r_{Pd}$, the number of water molecules is $n_w = n_w'/2.74$. Therefore, the density of a particle is approximately calculated by eq (12).

## 2.6 Addition of methyl viologen

Preliminary experiments were carried out in order to detect precursors to the fine particles: candidates of the precursors may be a cluster, for example, $(Pd_x)$ ( x may be 3 - 10 ) which is formed by the combination reaction of several atoms:

$$x\ Pd \rightarrow Pd_x$$

This precursor is known to be oxidized by methyl viologen, $MV^{2+}$ by:

$$Pd_x + MV^{2+} \rightarrow MV^{+}\cdot + Pd_x^{2+}$$

to form the MV semi-cation radical which strongly absorbs 600nm [3] .

Deaerated 8 ml of palladium sulfate (1.0mM, pH=0.43) solution was irradiated with 5 kGy, and the irradiated solution was added in nitrogen atmosphere to 8 ml of $MV^{2+}$ (1.0 mM aqueous solution) which had been dearated with nitrogen stream in advance. The mixture was immediately subjected to UV and DLS measurements. In order to detect the cluster which might be exist during irradiation, simultaneous irradiation was carried out on a solution containing Pd and $MV^{2+}$ (0.5mM + 0.5mM, pH=0.43) at dose of 5 kGy and the irradiated solution was immediately subjected to UV and DLS measurements after the irradiation was completed.

# 3. RESULTS and DISCUSSION

## 3.1 Turbidity and particle size as a function of time during and after irradiation

Figure 2A shows turbidity ( measured as optical density, O. D. at 700nm) of the solution as a function of time, where time zero is the time of initiation of irradiation. The turbidity increased with increasing dose, indicating that the amount of non-transparent particles formed increased with increasing dose. However, after 15 kGy irradiation, the turbidity did not seem to increase with increasing dose. Also the decay of turbidity of the irradiated solution was faster, suggesting that during irradiation, the

$$n_w' = (R/r_a)^3 \quad \alpha - n_{Pd}$$

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particle size and density increased to values large enough to precipitate more quickly. The turbidity decreased just after irradiation was terminated, and the rate of turbidity decrease increased with dose. This also means that the particle size and density increased during irradiation.

Figure 2B shows the optical density at 388nm, which is an absorption maximum of remaining palladium aquo-complex ion, as a function of time. The optical density at this wave length decreased a little at early stage after irradiation was completed, and then gradually decreased with time. This means that small amounts of the remaining pallladium ion is adsorbed by clusters or paticles.

In Fig. 3, average particle diameter measured by DLS and calculated using UNIMA was plotted as a function of time during and after irradiation. It is clearly shown that the particle size increased with increasing time during and after irradiation up to 10000 sec, and it is further noticed that the plots obtained at different doses came together to a rather narrow scattering range in this time range. After 10000 sec, the increase of particle size levels off for 1 - 2.5 kGy irradiation, while decrease of the particle size was observed for the solutions irradiated with larger doses, indicating that particles of larg size precipitate leaving small size particles, and the decrease was faster, the larger the dose. These phenomena were explained by that growth of the particle size occurred after irradiation, but more closely packed particles were formed during irradiation, and therefore the sedimentation rate is larger in the solution irradiated with larger doses.

## 3.2 Characteristic parameters of particles floating in the solution

Several sets of $\Delta$OD389, OD700, and D (=2r) taken at 300, 10000 and 30000 sec after irradiation taken from Figs. 2A, 2B, and 3 are shown in Table 1 and the results of calculation using these data are shown in Table 2.

The results of the calculation seem to give us rough image of shape and growth of particles in the solution. Take the result obtained for 1 kGy irradiation for example, the average density of particle including water, $d_w$ ,(3.61g/cm$^3$) decreases with time, the average number of Pd atoms ($0.3 \times 10^8$/particle ) in a particle increased to $13.8\times10^8$/particle, and the average number of particles in the solution ($9.5\times10^8$/cm$^3$) decreases to $0.2 \times10^8$/cm$^3$

with time, showing gradual growth of particles by the coagulation of the smaller particles to form bulky particles of low density. However, the calculations for the particles obtained by higher doses (>10 kGy) indicated that the density went up again with time and values at long elapsed time (10000 or 30000sec) gave unreasonably high values which are indicated by parentheses. This is because under these conditions, precipitate was observed at the bottom of the vessel and the assumption that all ions consumed are floating in the solution as non-transparent particles is no longer valid.

Sedimentation curves calculated using eq (5) on the basis of Stokes' law on the assumption that no particle growth occurs after irradiation are shown in Fig. 4 for the solutions irradiated with 1 kGy and 5 kGy, respectively. The observed decay is faster than that expected from the Stokes' law, indicating that the turbidity decay is resulted from the growth of the particle.

Scattered photon intensity is plotted as a function of time during and after the irradiation in Fig. 5 where it is noted that the intensity decreased with time, showing that the number of particles in the solution which scatter the light decreases with time. The shapes of the curves are similar to those obtained by the UV method (Fig. 2A).

In Figs. 6A and 6B, absorptions at 388nm and 700nm (turbidity) are plotted as a function of time after irradiation, one without agitation and the other, under continuous agitation with a magnetic stirrer during UV measurement, respectively. The decay of turbidity is faster when the solution was agitated continuously than that without agitation, showing that the agitation increases the number of collisions between the particles in the solution and favors the growth of particles shaking out the water molecules out of the cavities of the bulky palladium-water particles. The absorption at 388nm due to the remaining palladium ions decreased a little at very early stage and then slightly decreased with time, independent of with or without the agitation. This indicates that a slight amount of palladium ions are adsorbed by the palladium particles, but most of remaining palladium ion stably exists in the solution after irradiation.

### 3.3 Does supersonic agitation re-disperse once coagulated precipitates?

The following three figures relate to the experiment that was carried out

in order to determine whether supersonic agitation breaks once coagulated particles. In Fig. 7, the turbidity was plotted as a function of time after irradiation, and subsequent turbidity decay after every supersonic agitation. After the first supersonic agitation, turbidity recovered to the original value obtained immediately after irradiation and showed a shoulder at 10000 sec after the agitation, suggesting the presence of larger size and high density fraction of narrow distribution. After the second and third agitation, the turbidity no longer returned to the original value, but stage of small slope appeared in the curve, indicating that a part of the solid is dispersed by the agitation and that the dispersed particles may have fine and rather narrow distribution of diameter. The fraction of re-dispersed particle decreased with increasing number of cycles of agitation, showing that repeatedly agitated solid precipitates form rather concrete bodies which were no longer dispersed by the supersonic agitation. In Fig. 8, a similar plot was shown for scattered photon count as a function of time after irradiation, and after supersonic agitation of precipitated solid. Decay curves similar to the turbidity curves were obtained except those after the second and the fourth agitations, the former the larger recovery of photon intensity, and the latter, sharp decrease in the early time period. Without going detail to these disagreements, it is recognized that the repeated cycles of agitation and sedimentation squeezed out of water molecules out of loosely coupled palladium particles to form dense coagulated particles that are not dispersed by the supersonic agitation, confirming the observation made by turbidity measurements. This discussion is further confirmed by the plots of diameter as a function of time which are shown in Fig. 9, where the diameter of particle after irradiation is 400nm, increased with time to 800nm, and then levelled off. After agitation, the diameter of the particles decreased by the agitation is the same as that observed after irradiation, and then increased with time after agitations until the third agitation. After the fourth agitation, the diameter was 900nm and did not increased with time.

Figure 10A shows the turbidity decay curve obtained for the solution that was agitated by supersonic irradiation for 2 hours immediately after gamma-irradiation. In the decay curve, a shoulder appeared at 10000sec and a flat stage appeared after 20000 sec, indicating that the supersonic agitation resulted some change of particle size distribution, forming a fraction of large size, high density particles and a fraction of fine particles, which may be responsible for the shoulder and the flat stage, respectively. Figure 10B shows

the turbidity decay curve obtained for the solution which was agitated by supersonic irradiation for 25 hours without gamma-ray irradiation. Slightly white hazy appearance was recognized by careful visual inspection of the solution after the agitation. The turbidity observed was small and the solution turned colorless with complete disppearance of 388nm absorption after several hours. The decay curve indicates rapid decrease of turbidity, but species responsible for the turbidity and fate of palladium ion are not known.

### 3.4 Growth of particles in the solutions of different palladium sulfate concentrations

In Figs. 11A, 11B and 12, turbidity, optical density at 388nm, and average diameter, and scattering photon intensity were plotted as a function of time after irradiation for solutions of five different palladium ion concntrations, respectively. The dose was 5 kGy for all solutions (0.125, 0.25, 0.5, and 1.0mM, pH=0.43) except for the 0.0625 molar solution (dose: 2.4 kGy, pH=0.43). As shown in Fig. 11B, turbidity decreased with time for all solutions, and turbidity immediately after irradiation and rates of decay are higher for higher concentration of palladium ions. Average particle size was 250 nm for all solutions except for the 0.0625 molar solutions (200nm) , increased with time, and then decreased or levelled-off depending on the concentration (Fig. 12); decreased with time after a maximum value when the concentration is high as 0.5 or 1.0 mM, while it levelled-off when the concentration is low as 0.0625 or 0.0125 mM. Optical density at 388nm decreased slightly with time except for the 0.0625 solution, indicating that most of the remaining palladium ion exist stably in the solution. Using optical absorption data, turbidity data, and diameter at 300, 10000, and 30000 sec after irradiation taken from Figs 11A, 11B, and 12, and listed in Table 3, several parameters describing the particles and their growth were calculated and the results are listed in Table 4. Density, $d_w$ after 300 sec after irradiation was 5.30 g/cm$^3$ for 1mM solution, and decreased with decreasing concentration of palladium ion in the solution, and was 3.47g/cm$^3$ for 0.125mM solution. For 0.0625 mM solution with 2.4 kGy, it was even smaller ( 2.07 g/cm$^3$ ). Number of particles in 1 ml solution was $9 \times 10^8$ for 1mM solution and $6.6 \times 10^8$ for 0.125mM solution. Number of palladium atoms in a particle also decreased with decreasing concentration of palladium ion: $1.6 \times 10^8$ for 1 mM solution and $0.7 \times 10^8$ for 0.125 mM solution. Number of particles in solution and number of palladium atoms in a particle for 0.0625mM solution are larger (11

$\times 10^8$ ) and smaller ( 0.016 $\times 10^8$), respectively, than those obtained for 0.125 mM solution, perhaps because smaller palladium particles did not coagulate to form large particle at low concentration and low dose.

Figure 13 shows plots of scattered photon intensities as a function of time for solutions of different initial palladium ion concentrations. The intensities decreased with time showing that the particles that scatter the laser light decrease from the solutions, but the reason that higher counts were observed for 0.5 mM solution than those observed for 1 mM and 0.25mM solutions is not known.

As mentioned above, it was observed that the optical density at 388nm decreased rapidly with time for the solution containing 0.0625mM and irradiated with 2.4 kGy (Fig. 11B). The data are reproduced in Figs. 14A and 14B with the data obtained for the solution of the same concentration, but irradiated with 3 kGy. It is noticed that the optical denisty at 700nm obtained for the both solutions decayed similarly, but that at 388nm, the solution irradiated with 3 kGy did not decay as fast as that with 2.4 kGy. This means that at lower dose, there may exist reactive clusters and they may react with remaining palladium ion to form transparent colloids which do not contribute to the turbidity.

### 3.5 Palladium sulfate-silver sulfate solutions

Figure 15 shows turbidity of the solution of palladium sulfate-silver sulfate (0.5mM+0.5mM) as a function of time during and after irradiation with 2.5, 5, and 10 kGy. The turbidity immediately after the irradiation increased with increasing dose, indicating that the amount of metallic particles formed increased with increasing dose. For plots obtained with 2.5 and 5 kGy irradiations, the turbidity increased with time, reached a maximum, and then decreased with time. The increase of the turbidity at earlier period after irradiation indicates that clusters which do not absorb light at this wavelength (700nm) coagulate one another to form non-transparent aggregates. The decrease of turbidity after maximum with increasing decay rate with increasing dose indicates that the aggregates coagulate to form larger aggregates and go sedimentation. By the end of 10 kGy irradiation, most of clusters had already reacted to form aggregates, since no increase of turbidity was observed after the irradiation.

In Fig. 16, the particle size measured by DLS and calculated using UNIMA was plotted as a function of time during and after irradiation. It is shown that the particle size increased with increasing time during and after irradiation up to 20000 sec, and then leveled off; the leveling off value is higher for 10 kGy irradiation than for 2.5 kGy. The calculations to obtain parameters characterizing particles in the palladium sulfate solution were also done for the palladium sulfate-silver sulfate system. Data listed in Table 5 are sets of $\Delta$OD389, OD700, and D (=2 $\times$r) taken at 300, 10000 and 30000 sec after irradiation taken from Figs. 16 and 17, and results of the calculations using these data are shown in Table 6.

The results of the calculation indicate that (1) density of the particles did not change significantly with time, (2) the number of particles per 1ml solution decreased, and (3) the number of palladium and silver atoms per particle increased. For example, for solution irradiated with 5 kGy, the average density of particle including water, $d_w$, (2.45 g/cm$^3$) was still 2.69 practically unchanged after 30000 sec, the average number of Pd atoms ($3 \times 10^8$ /particle ) in a particle increased 20 times to $72 \times 10^8$ /particle, and the average number of particles in the solution ($1.8 \times 10^8$ / cm$^3$) decreases with time by one-fourtieth, showing gradual growth of particles by mutual get-together coagulation of the smaller particles forming large bulky particles. The density of the particles obtained for palladium-silver sulfate solution is smaller than the corresponding one obtained for palladium solution.

In Fig. 17, turbidity (O. D. at 700nm) is plotted as a function of time after supersonic agitation. Turbidity reached the original value immediately after irradiation except for the solution irradiated with 2.5 kGy, but no maximum was observed different from those obtained for the first decay curves (Fig. 16). This indicates that by supersonic agitation, precipitates were dispersed to fine particles, but not to cluster of a few atoms which does not absorb the light of the wavelength region studied and are supposed to be precursors of the particles.

Scattered photon intensity is plotted as a function of time during and after the irradiation in Fig. 18 where it is noted that the intensity decreased with time after maximum as observed in turbidity change (Fig. 15).

### 3.6 Changes caused by the addition of methyl viologen

Figure 19 shows change of electronic spectrum of $MV^{2+}$ solution ( 1 mM, pH=0.43 by sulfuric acid) with time after the $MV^{2+}$ solution was added with palladium sulfate solution (1.0mM, pH=0.43 ) which had been irradiated with 4.9 kGy (system a). The spectrum obtained 5 min. after mixing shows strong absorption due to $MV^{2+}$ at 260nm, an absorption maximum (410nm) due to palladium ion and broad absorption due to non-transparent solid particles, the last of which decreased with time, but no absorption of $MV^{+\cdot}$ semi-reduced cation was observed. Figure 20 shows spectrum of irradiated (4.9 kGy) mixed solution of palladium sulfate (1.0mM, pH=0.43 ) and $MV^{2+}$ ( 1 mM, pH=0.43 by sulfuric acid) (system b). In the spectrum of irradated mixture of palladium sulfate and $MV^{2+}$ a weak absorption due to an unknown product from irradiated $MV^{2+}$ appeared in addition to the strong absorption due to $MV^{2+}$ at 260nm, the weak absorption maximum due to palladium ion and the broad absorption due to non-transparent solid particles observed in the previous figure, but again no absorption of $MV^{+\cdot}$ semi-reduced cation was observed. The weak absorption is due to unknown product of irradiated $MV^{2+}$ which appeared in the spectrum of irradiated $MV^{2+}$ (Fig. 21).

The turbidity after irradiation was not the same for the two systems (a) and (b) and the system without any solutes other than palladium and sulfate ions(c). The turbidity for the three systems and decays with time are compared in Fig. 22. The turbidity after irradiation observed for (a) is the lowest as 0.12 about 1/2 of that for (c), but close to a half of that of irradiated 1 mM solution (d). Therefore, the mixing of 1 mM irradiated solution with 1 mM $MV^{2+}$ solution would seem to be simple dilution with inactive solvent. Perhaps, growth of palladium cluster is quite fast to delocalize their charges in the particle to stabilize by the time of the mixing (a few minutes), and therefore, the oxidation of the particles by $MV^{2+}$ was not observed in the present system. However, it is curious to note in Fig. 19 that the wavelength of absorption maximum 410 nm which is 12 nm red shifted from 398nm, which is observed for standard palladium sulfate solution, and that the absorption due to palladium remained in the solution (0.055) was higher than that expected for unirradiated 0.5 mM palladium sulfate solution ( $\varepsilon$ = 108.0 $M^{-1}$ [2]). The reason for this is not clear, it might be a reason that the presence of $MV^{2+}$ or its radiolytic products altered ligand configuration around the palladium to change absorption maximum and molar extinction coefficient.

In the simultaneous irradiation of palladium ion and $MV^{2+}$, higher turbidity than that for 0.5 mM palladium sulfate solution was observed for system (b) when 1 mM $MV^{2+}$ is present in the solution during irradiation, suggesting that $MV^{2+}$ may play a role as an effective electron carrier to palladium cluster ion at early stage of radiation chemical reaction of related species[3,4],

$$e_{aq}^{-} + MV^{2+} \rightarrow MV^{+\cdot}$$
$$MV^{+\cdot} + Pd_n \cdot Pd^{2+} \rightarrow Pd_n \cdot Pd^{+} + MV^{2+}$$
$$MV^{+\cdot} + Pd_n \cdot Pd^{+} \rightarrow Pd_{n+1} + MV^{2+}$$

Diameters of the particles are plotted in Fig. 23 as a function of time for the four solutions((a)-(d)). The diameter for solution (a) increased with time as the other three solutions, but the rate of increase was lower than the other three. This means that $MV^{2+}$ added in the solution may be adsorbed by the growing particles to retard the particles come together to coagulate. Scattered photon intensities are also plotted in Fig. 24 as a function of time for the four solutions. The scattering intensity observed for solution (a) decreased with time similarly to the solutions (b) and (d, 1.0 mM Pd solution, plotted on the right scale two times as much as on the left scale). To discuss the complex phenomena and difference from the results obtained by UV measurements, understanding of scattering phenomenon of this wavelength (623.7nm) will be necessary.

## 3.7 Relations among the scattering photon intensity, particle diameter, density, and other parameters of the solution

Scattering photon intensity (PI) may be related to the number of particles in the solution (n) but it may also be related to other parameters. According to a theory for Raileigh type scattering ($r << \lambda$), scattering intensity is said to be proportional to $r^6$ [5]. We made a few plots of PI against functions of n, particle radius (R), which are given as number of particles and diameter, respectively, in Tables 2, 4, and 6, and density ( $d_w$ :defined by eq (12), and d : defined by eq (9) in sec. 2.4. the values of $d_w$ are given as density in Tables 2, 4, and 6, but the values of d are not given in the table.) to find an empirical formula to relate the PI to other parameters, since the formula will give a useful information on particles in the solution from photon

intensity data.

In Fig. 25A, the PI is plotted as a function of $R^2n$. The plots (●and ■) give a linear line for the particles obtained for palladium sulfate solution ignoring two points which were obtained for extremely dilute palladium sulfate solutions. The plot (○) gives a line of different slope. The result may be reasonable because the PI may be proportional to the cross section of the particle as a scattering center, and to the number of the particles exist in the scattering zone. The different slopes for different material may be resulted from the difference of scattering coefficient of the material.

To find a formula which fits to materials on different lines, density of the materials was considered. The PI was plotted against $R^2nd_w$ and against $R^2nd$ instead of $R^2n$ in Fig. 25B and Fig. 25C, respectively. In these figures, plots are no longer on linear lines and in Fig. 25B, and the plots for the two materials are still on the separate curves, but as shown in Fig. 25C, the plots for the two materials lie on the one curve. This means that the density excluding water molecules is to be considered when one evaluates the PI from suspended solid particles of different materials. However, examination of the formula for wide range of the materials will be necessary for more confirming discussion.

## 4. CONCLUSIONS

Irradiation of deaerated aqueous solution of palladium sulfate by gamma rays resulted formation of water-filled bulky palladium particles of diameter of about 200nm, which grow by coagulation of the particles even after irradiation was terminated. Average density of the particles depends on concentration of the solution and dose, and the lowest average density was about 2 for particles of 200 nm diameter obtained from 0.06 mM solution by 2.4 kGy irradiation. The average densities of particles obtained for palladium sulfate-silver sulfate solutions were smaller than those obtained for corresponding palladium sulfate solutions, although the diameters are larger.

Supersonic agitation destroyed coagulated precipitates to fine particles, but not to very small particles of cluster size. Addition of methyl viologen retarded the growth of particles in solution, and enhanced the formation of particles when it was present in the solution during irradiation.

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Table 1 Data for calculation of the particle parameters
Initial concentration of palladium ion: 1 mM
Dose: variable

| Dose (kGy) | time (sec) | OD700 | Δod388 | D (nm) |
|---|---|---|---|---|
| | 300 | 0.12 | | 180 |
| 1 | 10000 | 0.105 | 0.005 | 650 |
| | 30000 | 0.075 | | 1000 |
| | 300 | 0.21 | | 220 |
| 2.5 | 10000 | 0.17 | 0.012 | 700 |
| | 30000 | 0.085 | | 1050 |
| | 300 | 0.26 | | 280 |
| 5 | 10000 | 0.15 | 0.028 | 750 |
| | 30000 | 0.05 | | 1000 |
| | 300 | 0.30 | | 400 |
| 10 | 10000 | 0.15 | 0.055 | 850 |
| | 30000 | 0.025 | | 1050 |
| | 300 | 0.32 | | 500 |
| 15 | 10000 | 0.13 | 0.083 | 1000 |
| | 30000 | 0.025 | | 650 |
| | 300 | 0.28 | | 750 |
| 20 | 10000 | 0.075 | 0.108 | 900 |
| | 30000 | 0.016 | | 375 |

Table 2 Parameters describing particles and their growth

| Dose (kGy) | time (sec) | density (g/cm³) | particles ×10⁸/ml soln | Pd atoms ×10⁸/particle | -[Pd²⁺] (mM) | diamter (nm) |
|---|---|---|---|---|---|---|
| | 300 | 3.61 | 9.5 | 0.29 | | 180 |
| 1 | 10000 | 2.51 | 0.65 | 4.3 | 0.046 | 650 |
| | 30000 | 2.45 | 0.20 | 13.8 | | 1000 |
| | 300 | 3.98 | 10.1 | 0.66 | | 220 |
| 2.5 | 10000 | 2.74 | 0.84 | 7.95 | 0.111 | 700 |
| | 30000 | 2.9 | 0.21 | 32.6 | | 1050 |
| | 300 | 5.09 | 7.32 | 2.13 | | 280 |
| 5 | 10000 | 3.78 | 0.66 | 23.6 | 0.259 | 750 |
| | 30000 | 5.58 | 0.14 | 111.3 | | 1000 |
| | 300 | 5.83 | 4.0 | 7.72 | | 400 |
| 10 | 10000 | 5.08 | 0.52 | 59.6 | 0.509 | 850 |
| | 30000 | (15. ) | (0.06) | (475.) | | 1050 |
| | 300 | 6.42 | 2.66 | 17.4 | | 500 |
| 15 | 10000 | 6.46 | 0.33 | 140. | 0.769 | 1000 |
| | 30000 | (34. ) | (0.17) | (274.) | | 650 |
| | 300 | 6.21 | 1.08 | 56. | | 750 |
| 20 | 10000 | (12.5) | (0.25) | (241.) | 1.00 | 900 |
| | 30000 | (112. ) | (0.33) | (184.) | | 375 |

Table 3 Data for calculation of the particle parameters
Dose: 5 kGy (for 0.0625 mM solution, 2.4 kGy)
Concentration: variable

| Conc (mM) | time (sec) | OD700 | ΔOD388 | D (nm) |
|---|---|---|---|---|
| | 300 | 0.25 | | 250 |
| 1 | 10000 | 0.17 | 0.026 | 750 |
| | 30000 | 0.04 | | 1000 |
| | 300 | 0.22 | | 250 |
| 0.5 | 10000 | 0.15 | 0.023 | 750 |
| | 30000 | 0.05 | | 1000 |
| | 300 | 0.19 | | 250 |
| 0.25 | 10000 | 0.15 | 0.012 | 750 |
| | 30000 | 0.08 | | 1150 |
| | 300 | 0.175 | | 250 |
| 0.125 | 10000 | 0.105 | 0.0085 | 750 |
| | 30000 | 0.08 | | 1050 |
| | 300 | 0.28 | | 200 |
| 0.0625 | 10000 | 0.075 | 0.0003 | 650 |
| | 30000 | 0.016 | | 900 |

Table 4 Parameters describing particles and their growth

| Conc (mM) | time (sec) | density (g/cm$^3$) | particles $\times 10^8$/ml soln | Pd atoms $\times 10^8$/particle | $-[Pd^{2+}]$ (mM) | diamter (nm) |
|---|---|---|---|---|---|---|
| | 300 | 5.30 | 8.92 | 1.63 | | 250 |
| 1 | 10000 | 3.49 | 0.73 | 19.8 | 0.243 | 750 |
| | 30000 | 6.11 | 0.11 | 129. | | 1000 |
| | 300 | 5.22 | 8.1 | 1.58 | | 250 |
| 0.5 | 10000 | 3.47 | 0.66 | 19.4 | 0.213 | 750 |
| | 30000 | 4.94 | 0.14 | 92.63 | | 1000 |
| | 300 | 3.89 | 7.22 | 0.93 | | 250 |
| 0.25 | 10000 | 2.77 | 0.66 | 10.1 | 0.111 | 750 |
| | 30000 | 2.87 | 0.16 | 41.3 | | 1150 |
| | 300 | 3.47 | 6.6 | 0.72 | | 250 |
| 0.125 | 10000 | 2.56 | 0.64 | 7.4 | 0.079 | 750 |
| | 30000 | 2.68 | 0.19 | 24.4 | | 1050 |
| | 300 | 2.07 | 10.6 | 0.016 | | 200 |
| 0.0625 | 10000 | 2.04 | 0.65 | 0.26 | 0.003 | 650 |
| | 30000 | 2.04 | 0.27 | 0.63 | | 900 |

Table 5 Data for calculation of the particle parameters
Initial concentration of palladium ion: 0.5 mM
Initial concentration of silver ion: 0.5 mM
Dose: variable

| Dose (kGy) | time (sec) | OD700 | ΔOD388 | D (nm) |
|---|---|---|---|---|
| | 300 | 0.20 | | 400 |
| 2.5 | 10000 | 0.23 | 0.009 | 1000 |
| | 30000 | 0.09 | | 1300 |
| | 300 | 0.35 | | 630 |
| 5 | 10000 | 0.30 | 0.011 | 1200 |
| | 30000 | 0.07 | | 1500 |
| | 300 | 0.54 | | 600 |
| 10 | 10000 | 0.20 | 0.025 | 1400 |
| | 30000 | 0.06 | | 2300 |

Table 6 Parameters describing particles and their growth
(palladium sufate-silver sulfate)

| Dose (kGy) | time (sec) | density ($g/cm^3$) | particles $\times 10^8$/ml soln | Ag+Pd atoms $\times 10^8$/particle | $-[Pd^{2+}]$ (mM) | diamter (nm) |
|---|---|---|---|---|---|---|
| | 300 | 2.86 | 2.94 | 1.71 | | 400 |
| 2.5 | 10000 | 2.31 | 0.52 | 9.58 | 0.083 | 1000 |
| | 30000 | 2.52 | 0.14 | 35.6 | | 1300 |
| | 300 | 2.45 | 1.78 | 3.5 | | 630 |
| 5 | 10000 | 2.26 | 0.44 | 13.9 | 0.102 | 1200 |
| | 30000 | 2.69 | 0.08 | 72.8 | | 1500 |
| | 300 | 2.82 | 2.52 | 5.5 | | 600 |
| 10 | 10000 | 2.68 | 0.24 | 58.1 | 0.231 | 1400 |
| | 30000 | 3.18 | 0.03 | 449. | | 2300 |

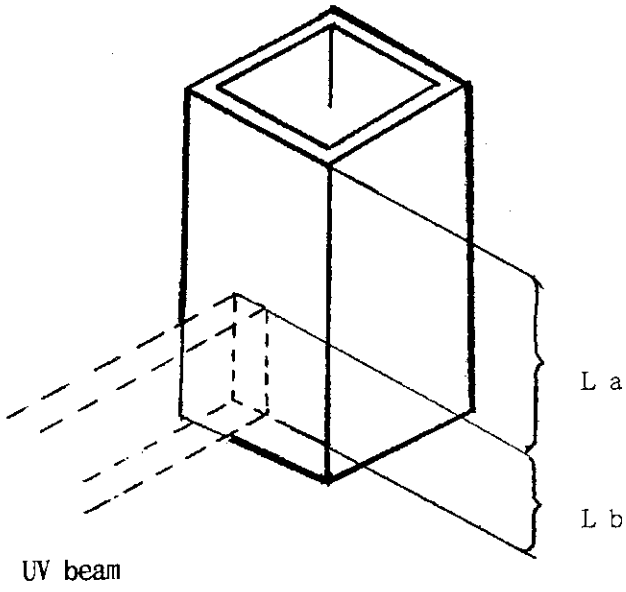


Fig. 1A Cuvette for UV measurements and beam position.

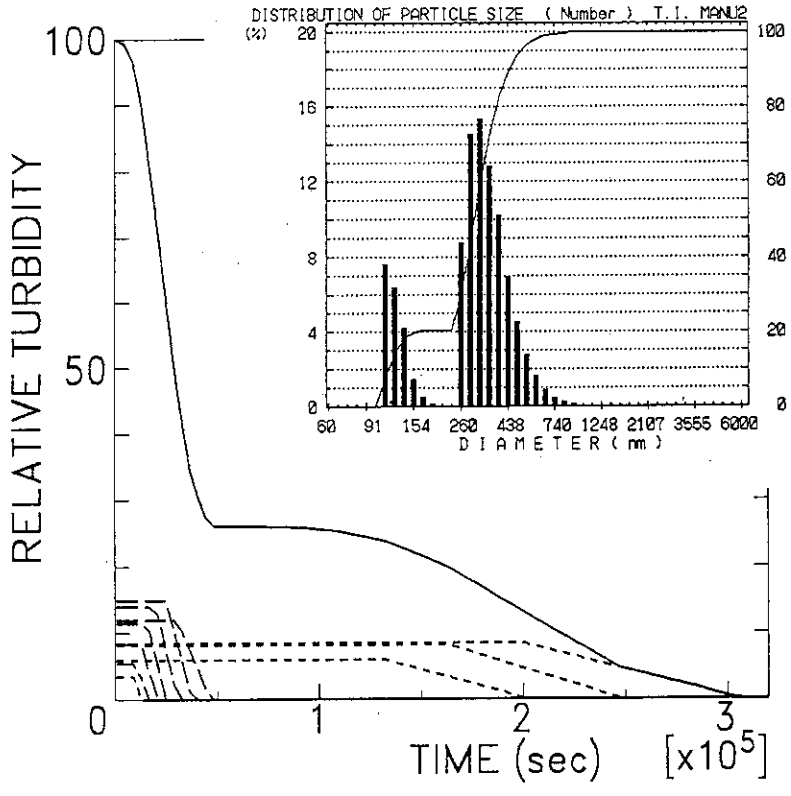


Fig. 1B Distribution of particle size and turbidity change with time calculated by Stokes' law and the size distribution; dose, 1 kGy; $[Pd^{2+}]$ : 1 mM, pH = 0.43.

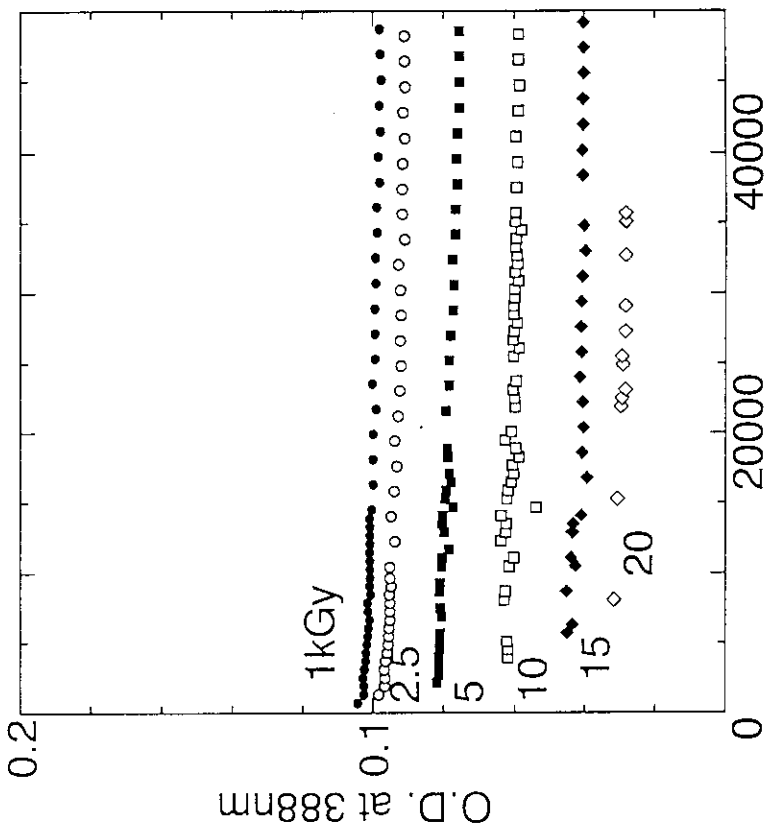


Fig. 2B O. D. at 388 nm as a function of time during and after irradiation; numerals in the figure denote dose in kGy; $[Pd^{2+}]$ : 1 mM, pH = 0.43.

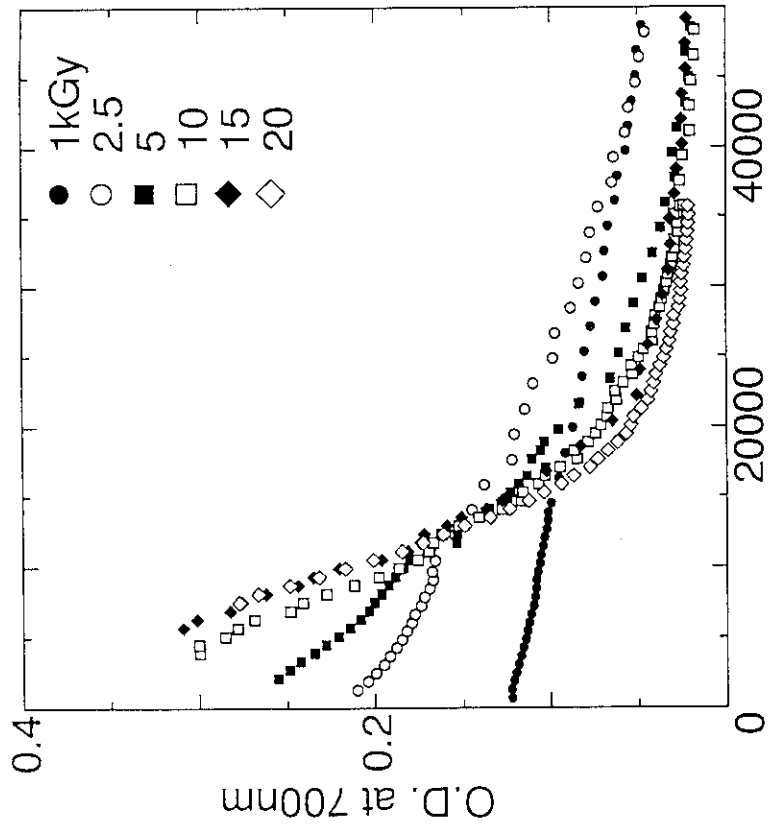


Fig. 2A O. D. at 700 nm (Turbidity) as a function of time during and after irradiation; numerals in the figure denote dose in kGy; $[Pb^{2+}]$ : 1 mM, pH = 0.43.

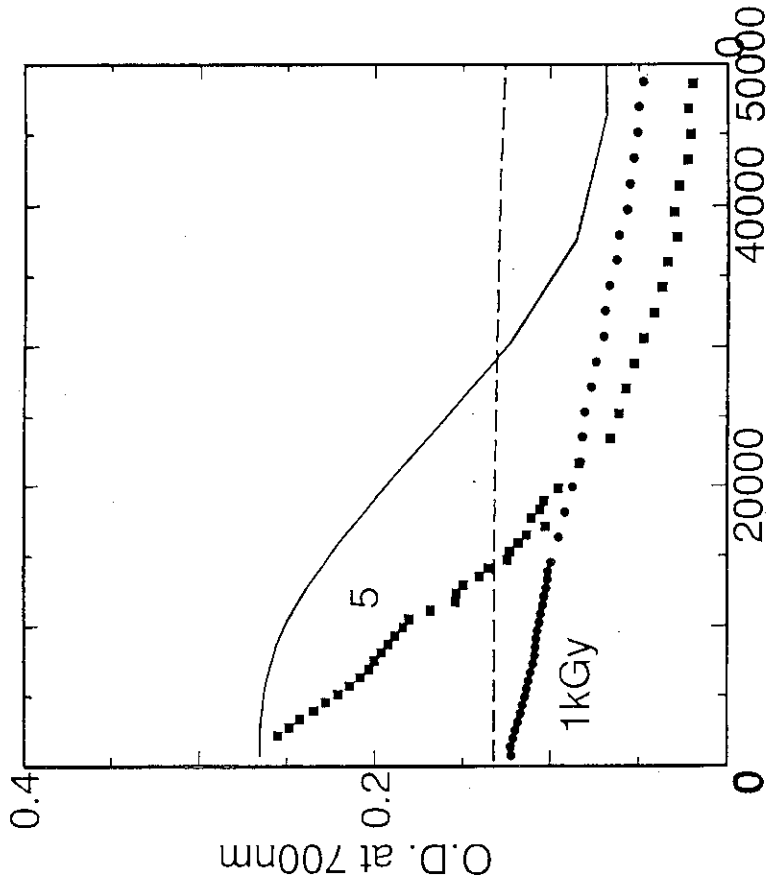


Fig. 4 Change of turbidity with time: —— ■, 5 kGy; ····· ●, 1 kGy irradiation; lines denote calculated values.

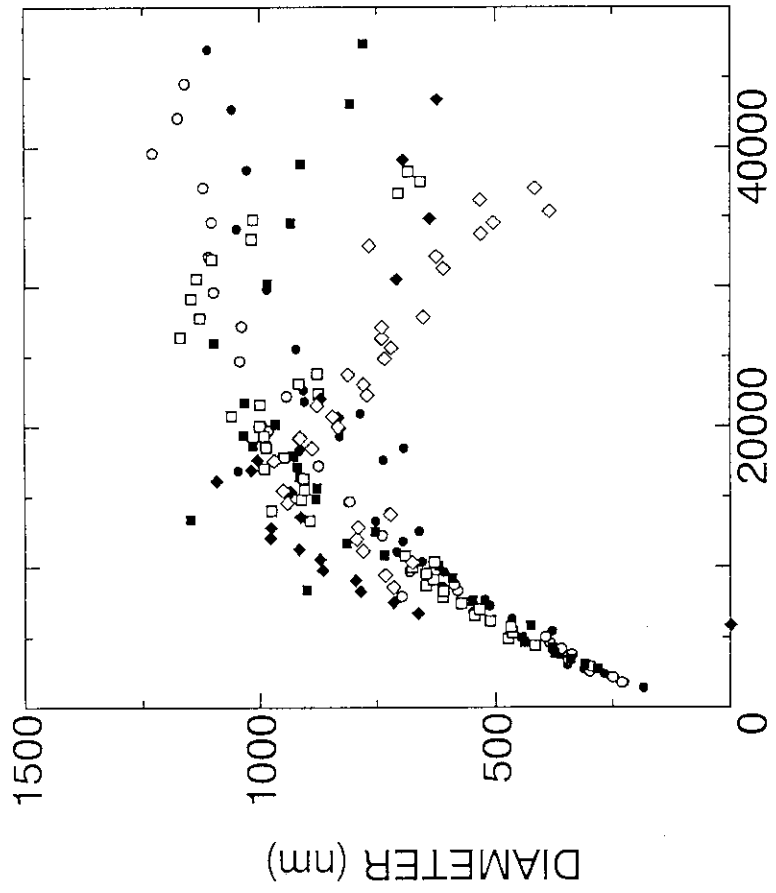


Fig. 3 Diameter of particles as measured by DLS method; ● 1; ○ 2.5; ■ 5; □ 10; ◆ 15; ◇ 20 kGy; $[Pd^{2+}]$ : 1 mM, pH = 0.43.

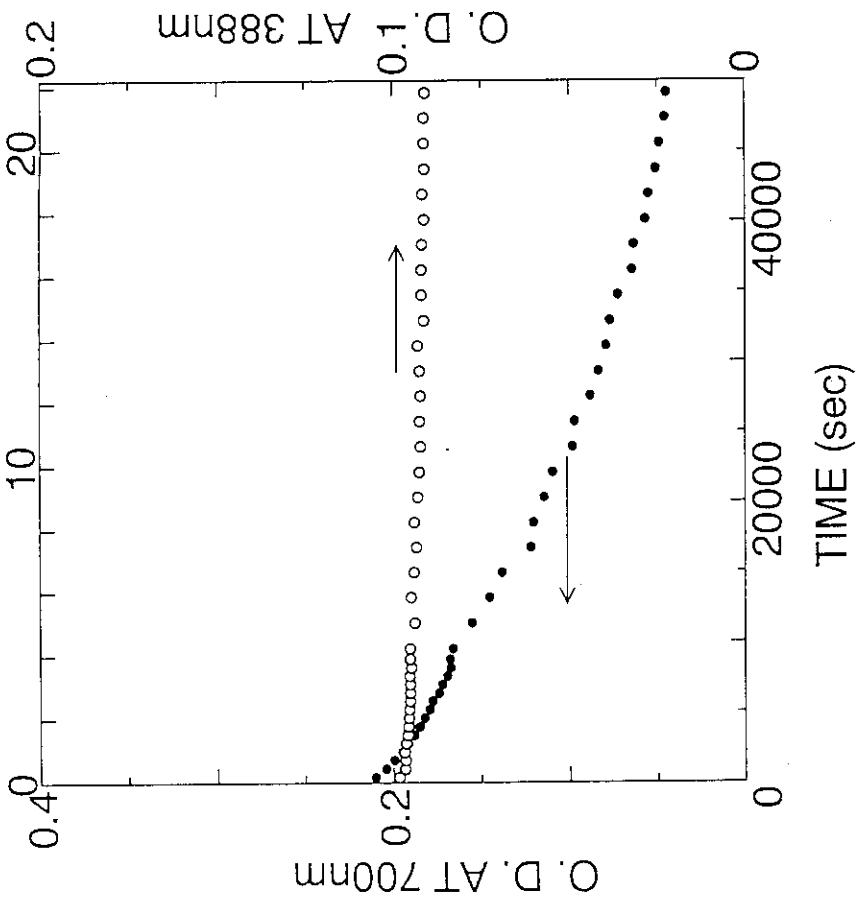


Fig. 6A Turbidity (O. D. at 700 nm) as a function of time after irradiation; Dose, 2.5 kGy, ; $[Pd^{2+}]$ : 1 mM, pH = 0.43; without agitation.

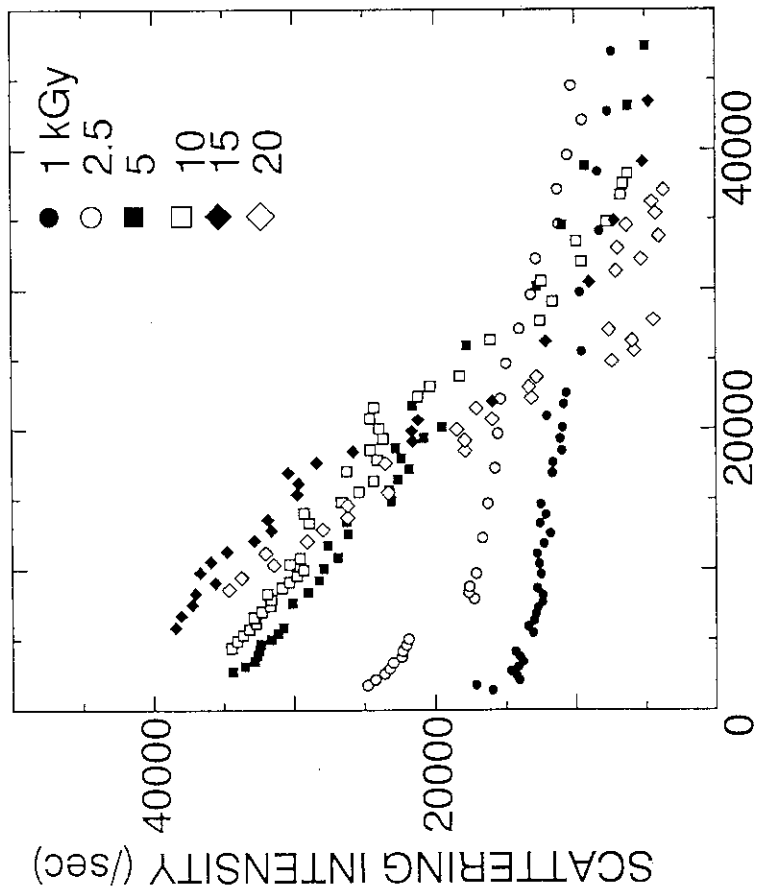


Fig. 5 Photon scattering intensity as a function of time during and after irradiation; numerals in the figure denote dose in kGy; $[Pd^{2+}]$ : 1 mM, pH = 0.43.

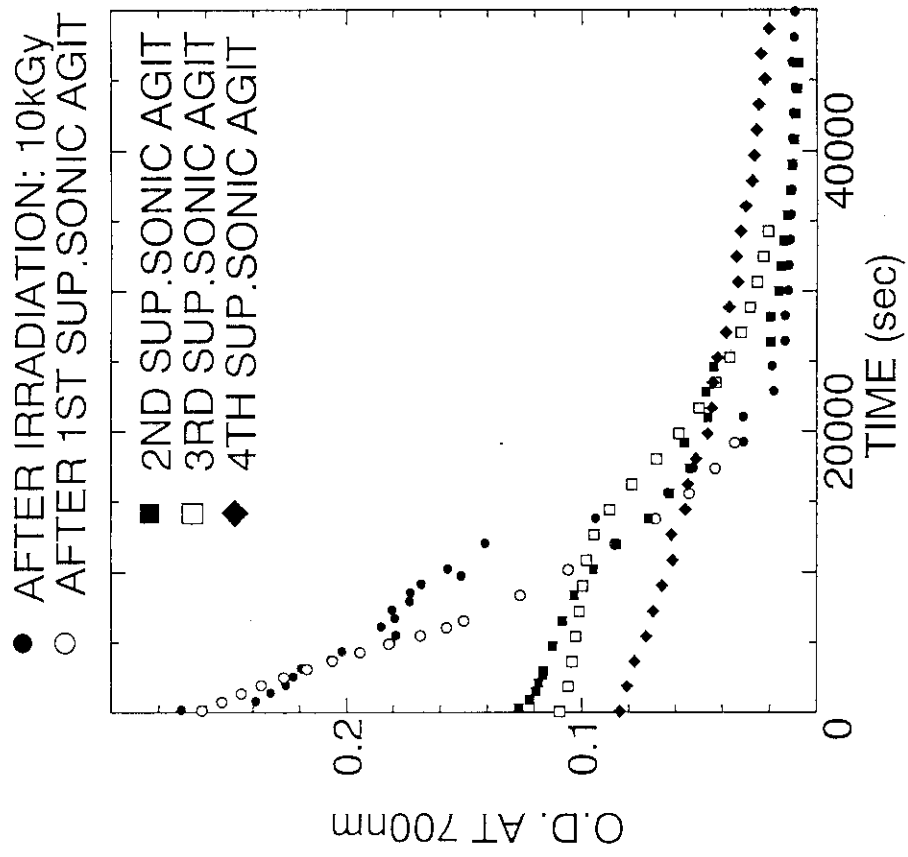


Fig. 7 Turbidity (O. D. at 700 nm) as a function of time after irradiation and after every repeated supersonic agitation.; dose: 10 kGy, $[Pd^{2+}]$ : 1 mM, pH: 0.43.

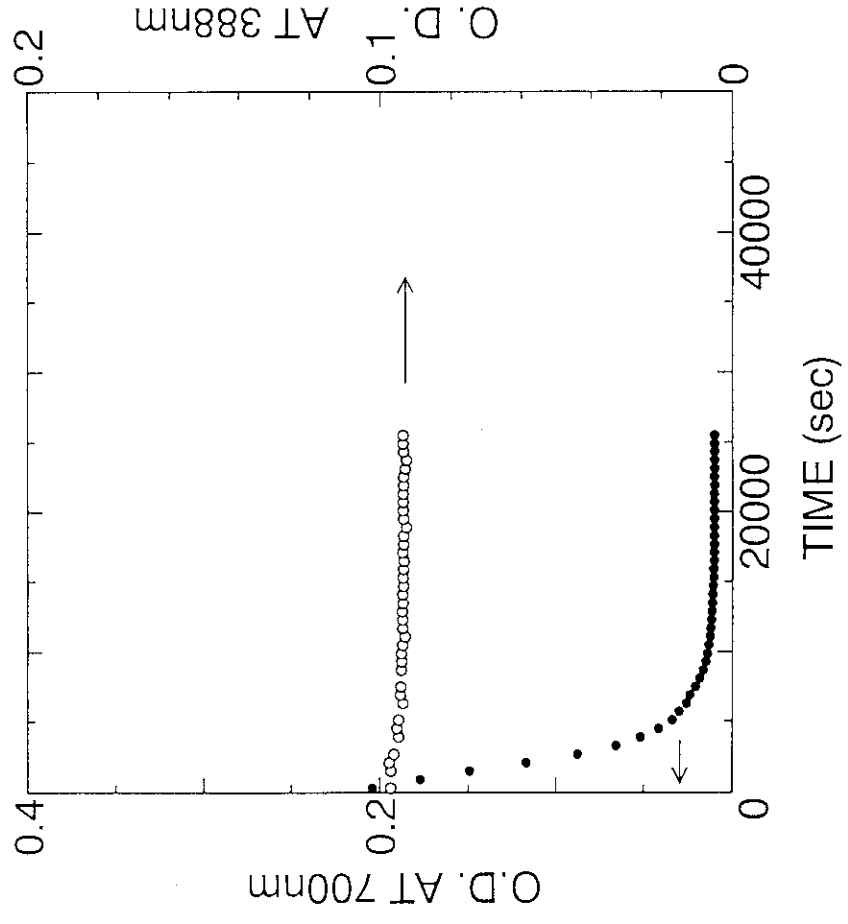


Fig. 6B O. D. at 388 nm as a function of time after irradiation; Dose, 2.5 kGy. ; $[Pd^{2+}]$ : 1 mM, pH = 0.43; agitated by magnetic stirrer.

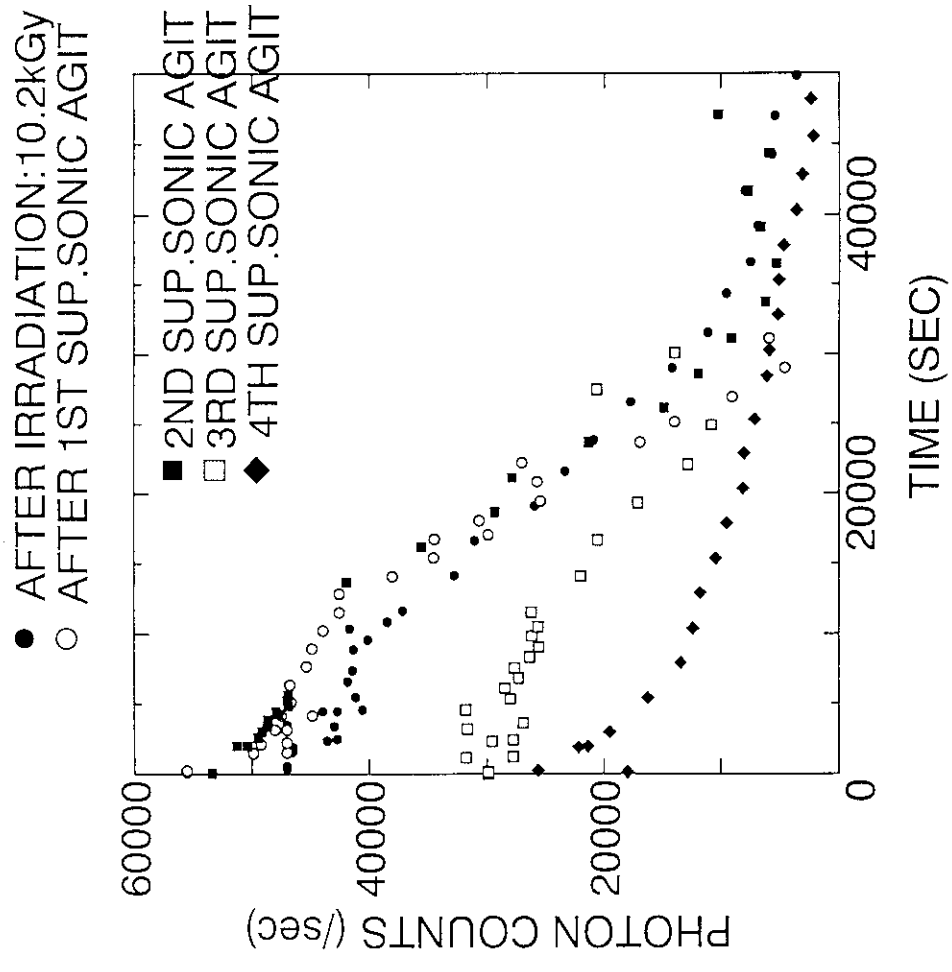


Fig. 8 Photon scattering intensity as a function of time after irradiation and after every repeated supersonic agitation.; dose: 10 kGy, $[Pd^{2+}]$ : 1 mM, pH: 0.43.

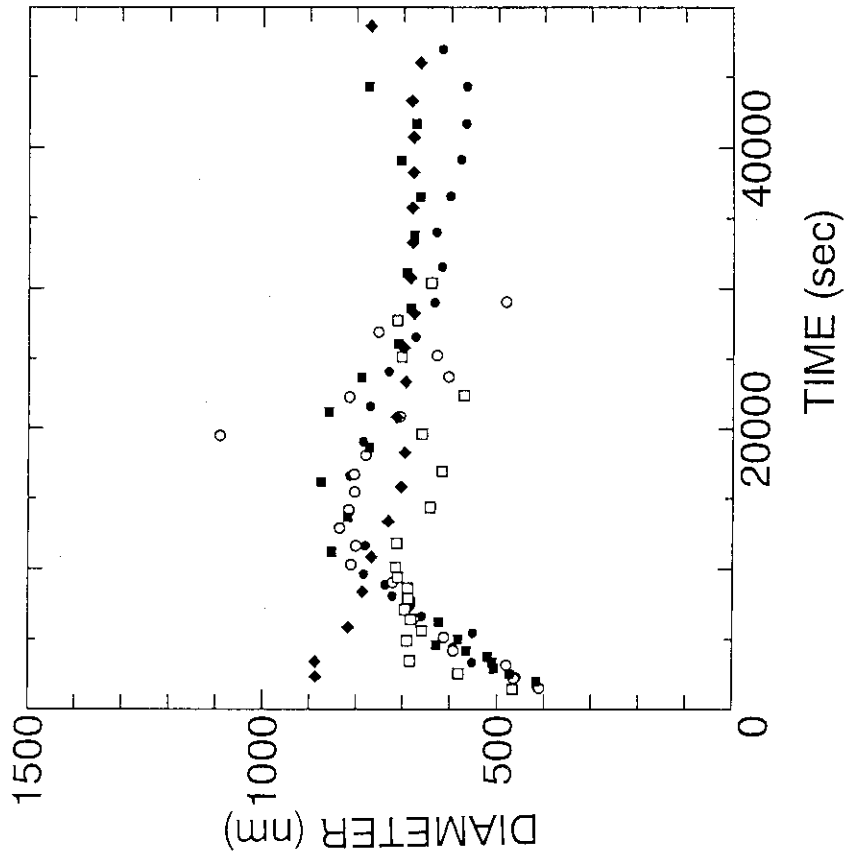


Fig. 9 Average diameter of particles as a function of time after irradiation and after every repeated supersonic agitation.; dose: 10 kGy, $[Pd^{2+}]$ : 1 mM, pH: 0.43.

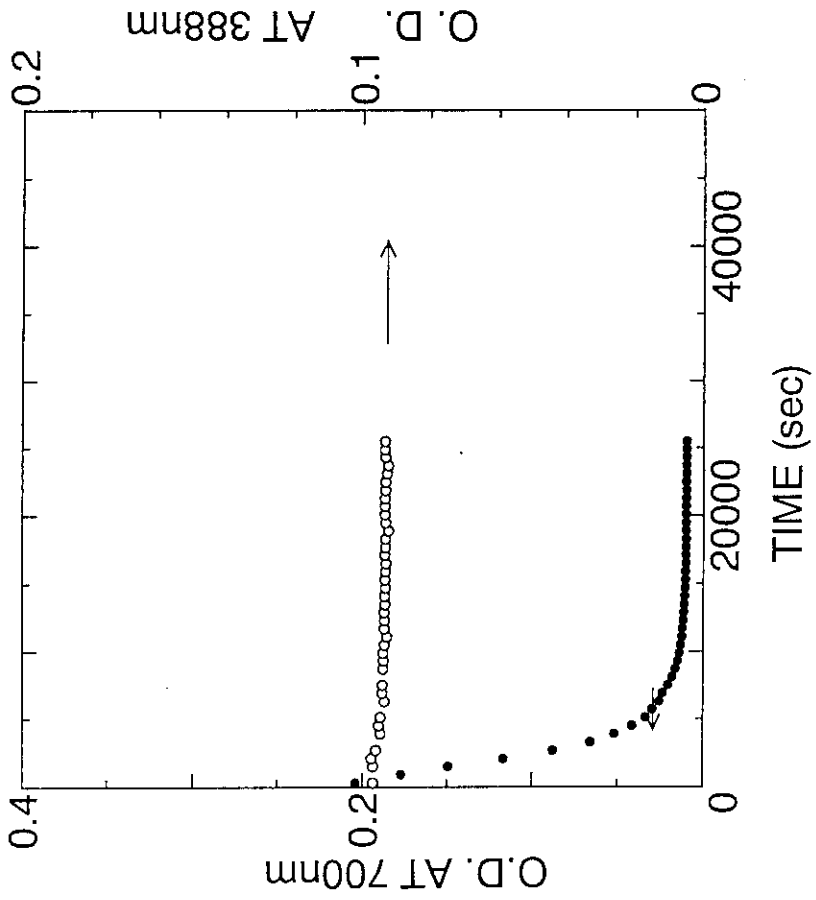


Fig. 10B Turbidity (●) and O. D. at 388 nm (○) as a function of time after super-sonic agitation for 25 hrs without gammaray irradiation.

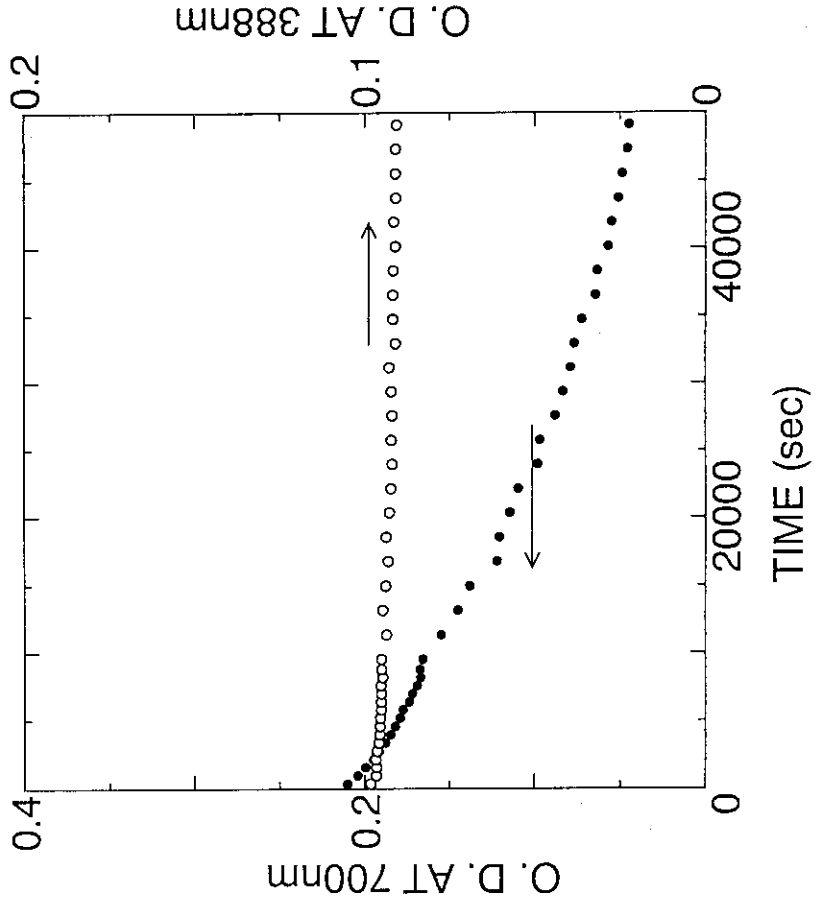


Fig. 10A Turbidity (●) and O. D. at 388 nm (○) as a function of time after super-sonic agitation (2 hrs) subsequently after irradiation (10 kGy) .

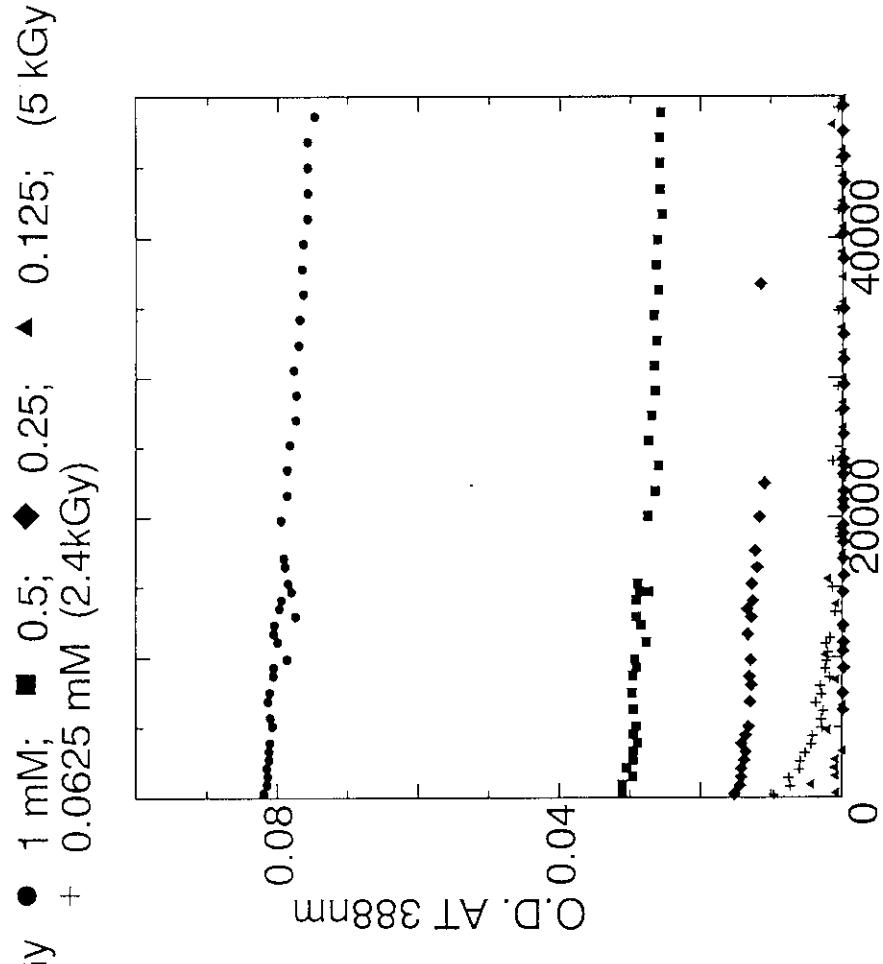


Fig. 11B O. D. at 388 nm as a function of time after irradiation; (●) dose: 5 kGy, $[Pd^{2+}]$ : 1 mM; (■) dose: 5 kGy, $[Pd^{2+}]$: 0.5 mM; (◆) dose: 5 kGy, $[Pd^{2+}]$ : 0.25 mM; (▲) dose : 5 kGy, $[Pd^{2+}]$ : 0.125 mM; (+) dose: 2.4 kGy, $[Pd^{2+}]$ : 0.0625 mM; pH: 0.43.

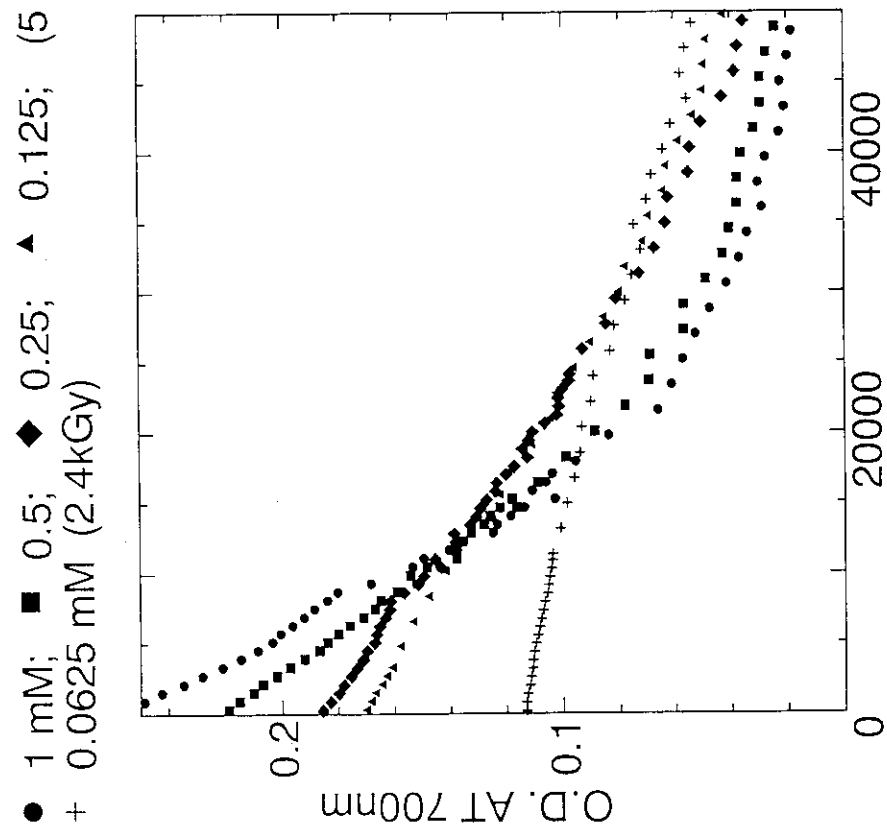


Fig. 11A Turbidity (O. D. at 700 nm) as a function of time after irradiation; (●) dose: 5 kGy, $[Pd^{2+}]$ : 1 mM; (■) dose: 5 kGy, $[Pd^{2+}]$ : 0.5 mM; (◆) dose: 5 kGy, $[Pd^{2+}]$ : 0.25 mM; (▲) dose: 5 kGy, $[Pd^{2+}]$ : 0.125 mM; (+) dose: 2.4 kGy, $[Pd^{2+}]$ : 0.0625 mM; pH: 0.43.

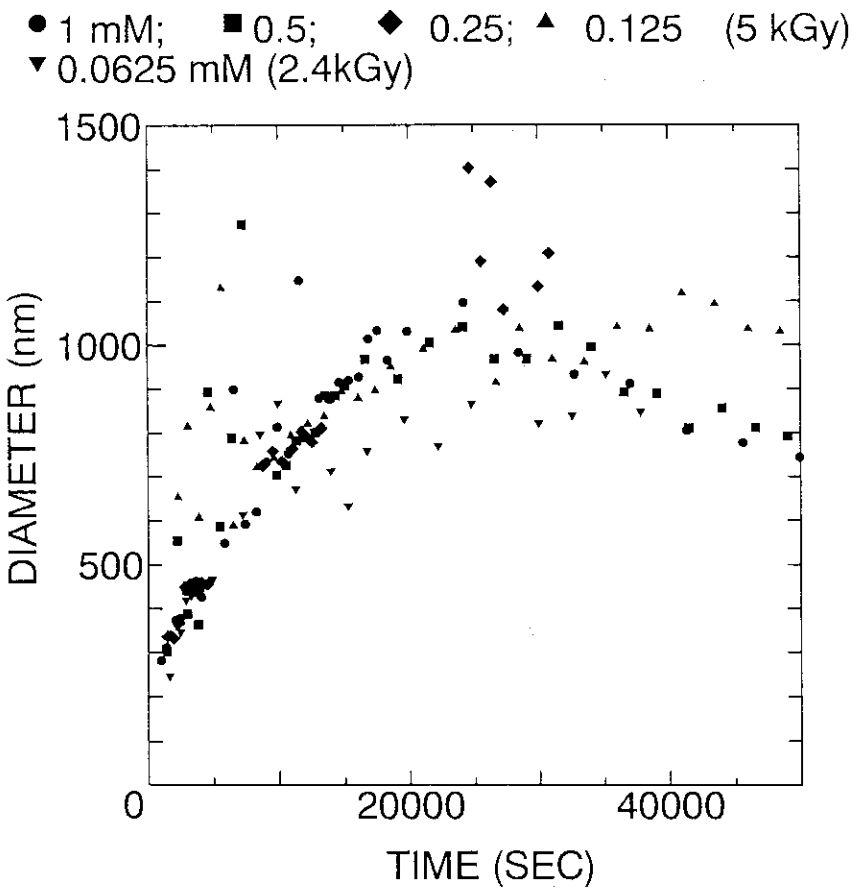


Fig. 12 Average diameter of particles as a function of time after irradiation; (●) dose: 5 kGy, [$Pd^{2+}$] : 1 mM; (■) dose: 5 kGy, [$Pd^{2+}$] : 0.5 mM; (◆) dose: 5 kGy,[$Pd^{2+}$] : 0.25 mM; (▲) dose: 5 kGy, [$Pd^{2+}$] : 0.125 mM; (+) dose: 2.4 kGy, [$Pd^{2+}$] : 0.0625 mM; pH: 0.43.

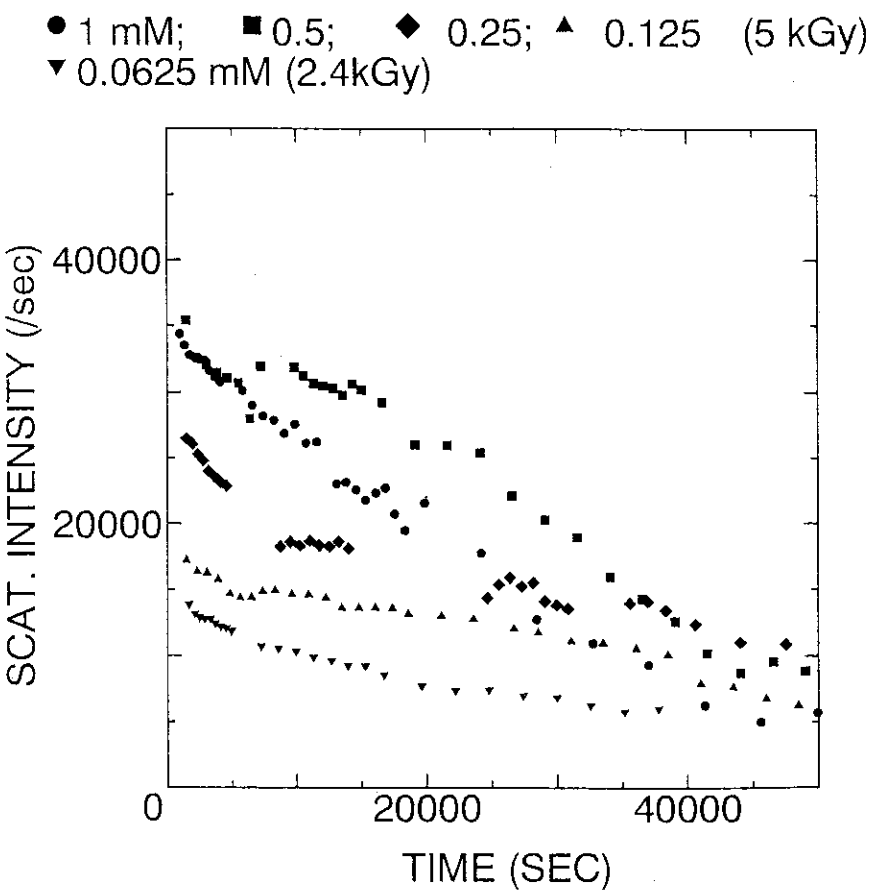


Fig. 13 Photon scattering intensity as a function of time after irradiation; (●) dose: 5 kGy, [$Pd^{2+}$] : 1 mM; (■) dose: 5 kGy, [$Pd^{2+}$] : 0.5 mM; (◆) dose: 5 kGy, [$Pd^{2+}$] : 0.25 mM; (▲) dose: 5 kGy, [$Pd^{2+}$] : 0.125 mM; (+) dose: 2.4 kGy, [$Pd^{2+}$] : 0.0625 mM; pH: 0.43.

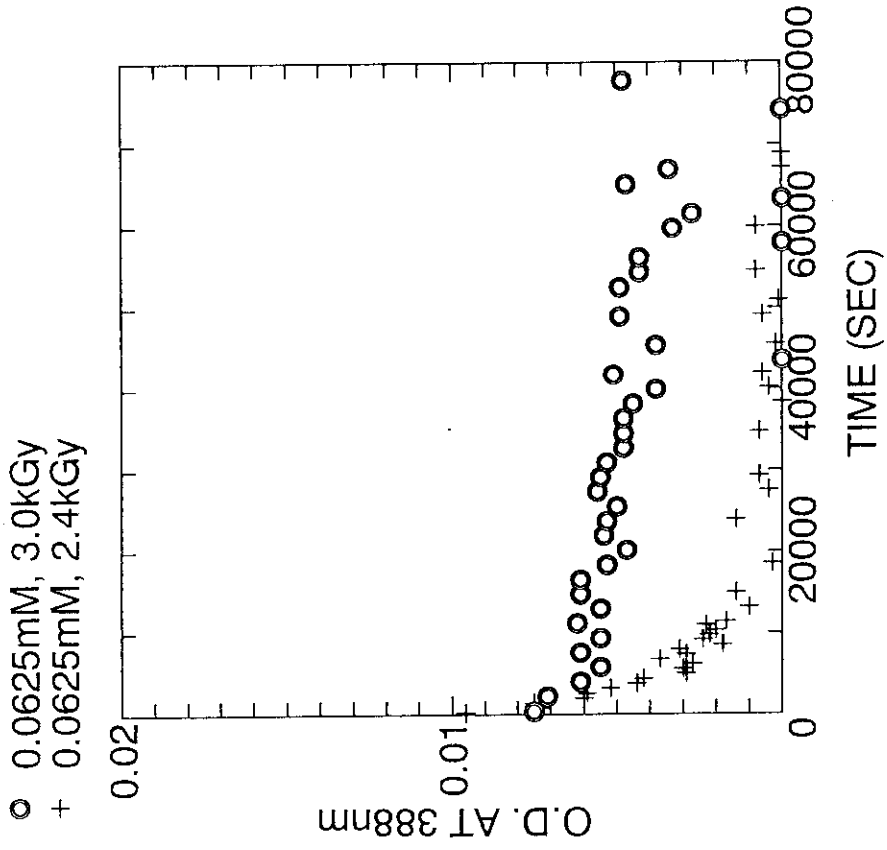


Fig. 14B O. D. at 388 nm as a function of time after irradiation; $[Pd^{2+}]$ : 0.0625 mM; pH: 0.43; (+) dose: 2.4 kGy, and (◎) dose: 3 kGy.

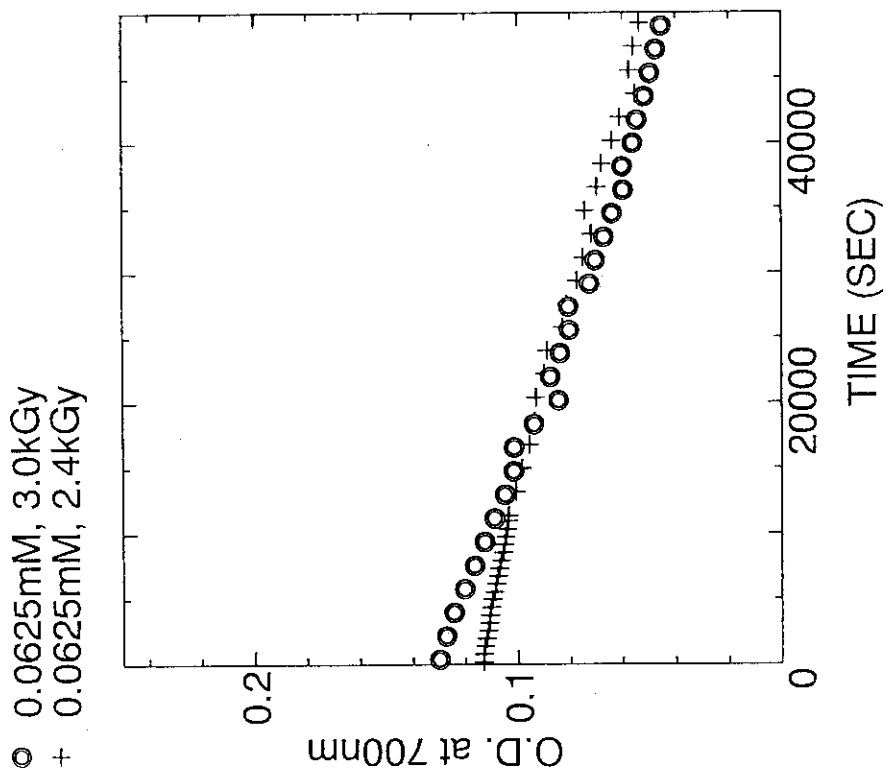


Fig. 14A O. D. at 700 nm as a function of time after irradiation; $[Pd^{2+}]$ : 0.0625 mM; pH: 0.43; (+) dose: 2.4 kGy, and (◎) dose: 3 kGy.

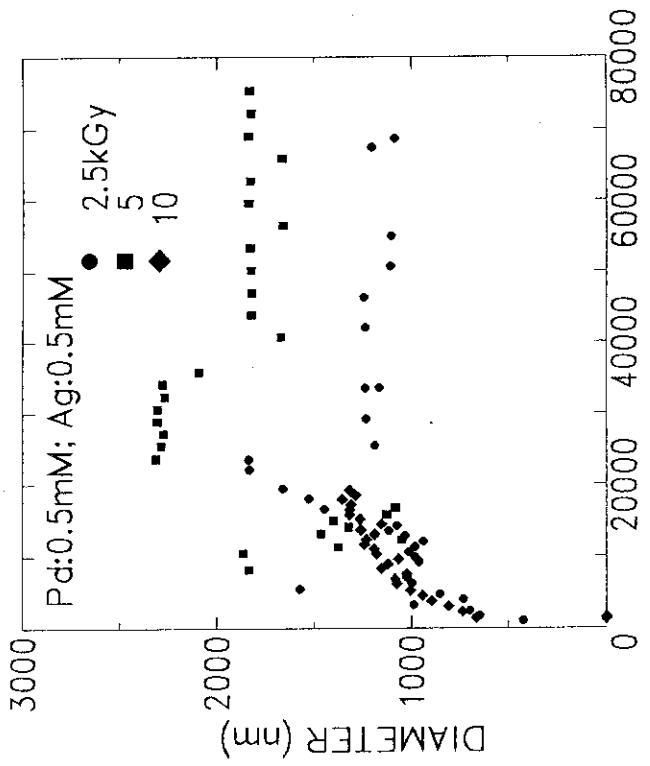


Fig. 16 Average diameter of particles as a function of time after irradiation for palladium sulfate-silver sulfate solution; $[Pd^{2+}]$ : 0.5 mM, $[Ag^{+}]$ : 0.5 mM; pH: 0.43; (●) dose: 2.5 kGy; (■) 5 kGy; (◆) 10 kGy.

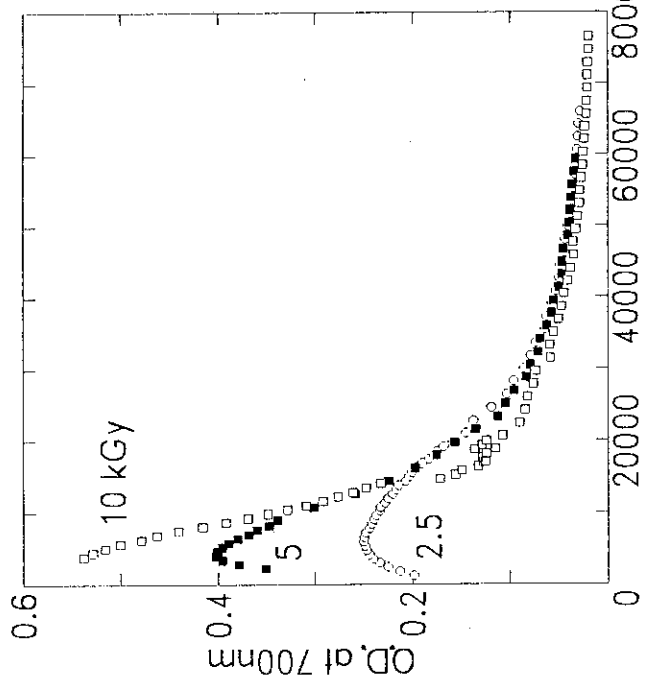


Fig. 15 Turbidity (O. D. at 700 nm) as a function of time after irradiation for palladium sulfate-silver sulfate solution; $[Pd^{2+}]$ : 0.5 mM, $[Ag^{+}]$ : 0.5 mM; pH: 0.43; (○) dose: 2.5 kGy; (■) 5 kGy; (□) 10 kGy.

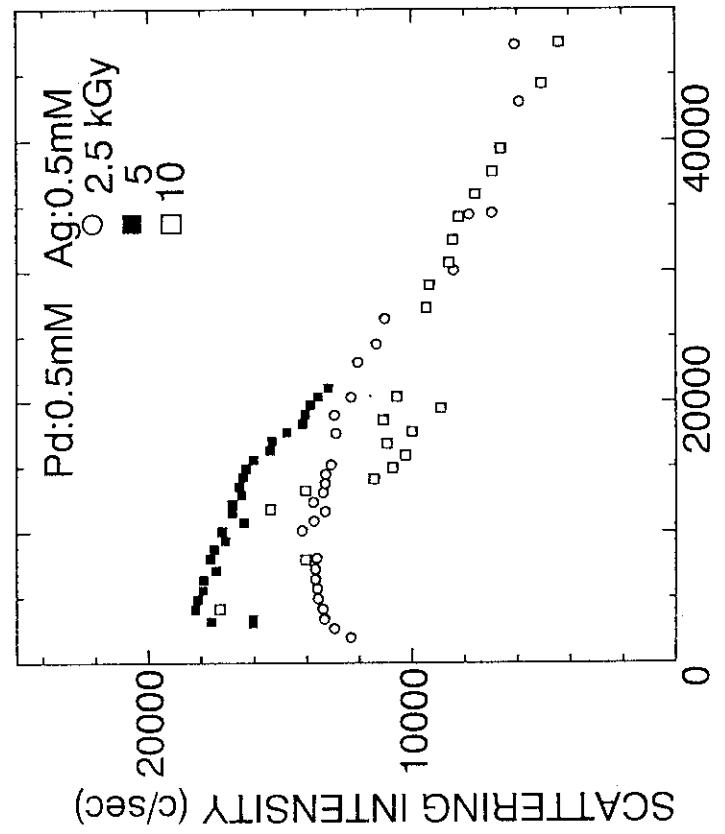


Fig. 18 Photon scattering intensity as a function of time after irradiation for palladium sulfate-silver sulfate solution; $[Pd^{2+}]$ : 0.5 mM, $[Ag^{+}]$ : 0.5 mM; pH: 0.43; (●) dose: 2.5 kGy; (■) 5 kGy; (◆) 10 kGy.

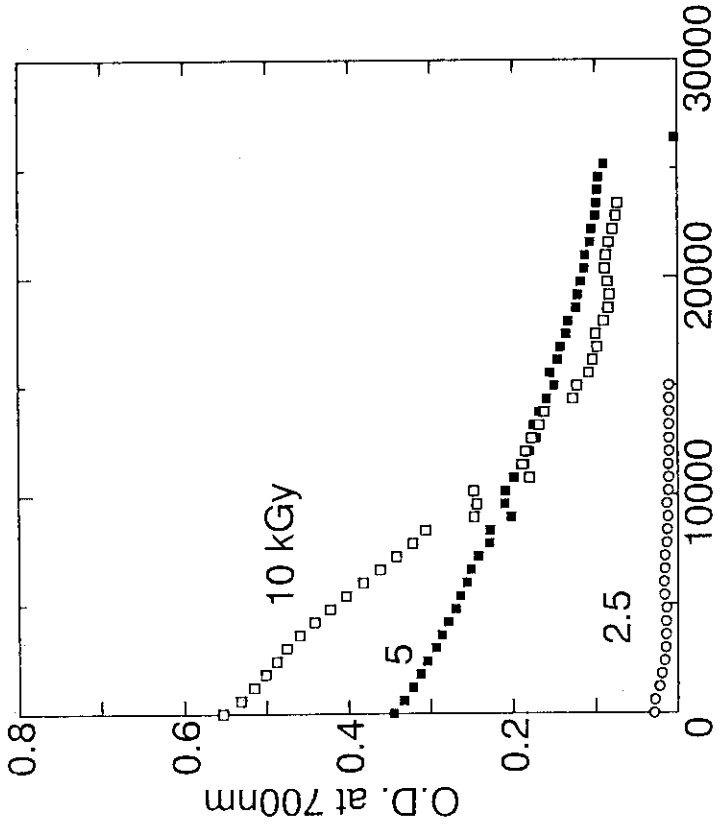


Fig. 17 Turbidity (O. D. at 700 nm) as a function of time after supersonic agitation (after irradiation, precipitation) for palladium sulfate-silver sulfate solution; $[Pd^{2+}]$ : 0.5 mM, $[Ag^{+}]$ : 0.5 mM, pH: 0.43; (○) dose: 2.5 kGy; (■) 5 kGy; (□) 10 kGy.

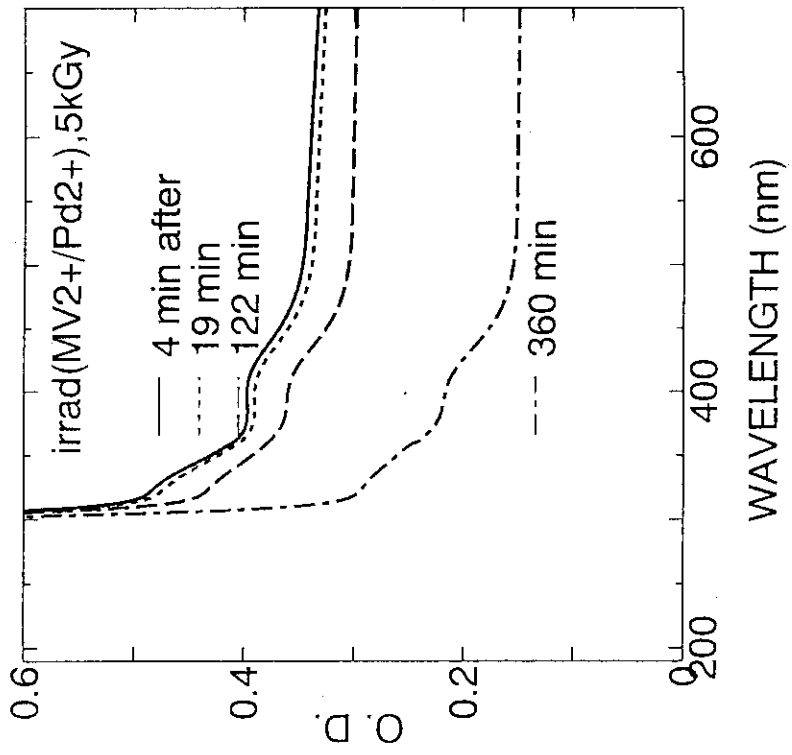


Fig. 20 Change of electronic spectrum of $MV^{2+}$ + palladium sulfate (0.5 mM + 0.5 mM, pH: 0.43) solution after irradiation.

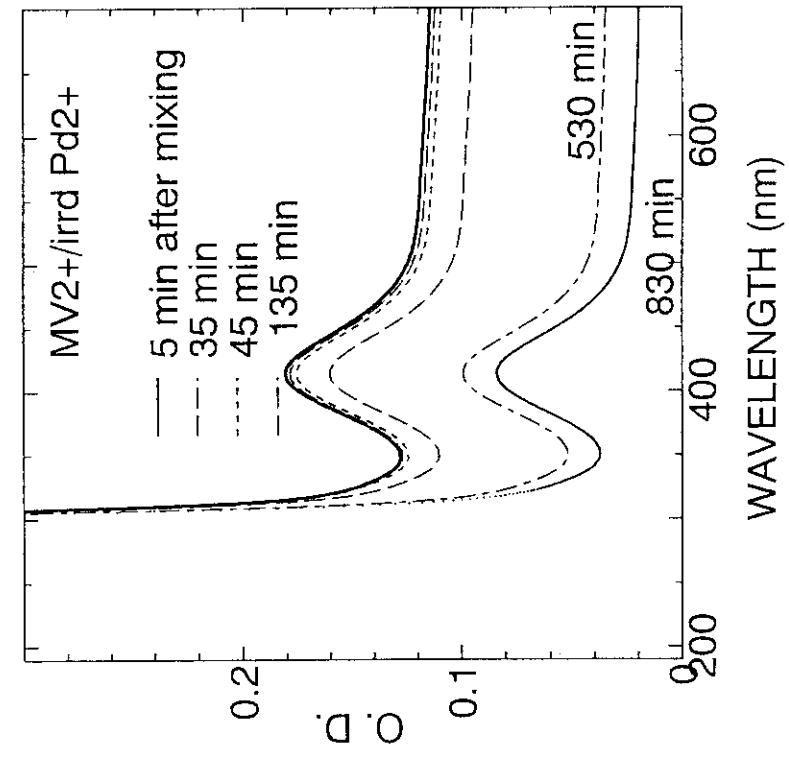


Fig. 19 Change of electronic spectrum of $MV^{2+}$ solution (1 mM, pH: 0.43) after mixing with irradiated palladium sulfate solution (1 mM, pH: 0.43) a few minutes after the irradiation.

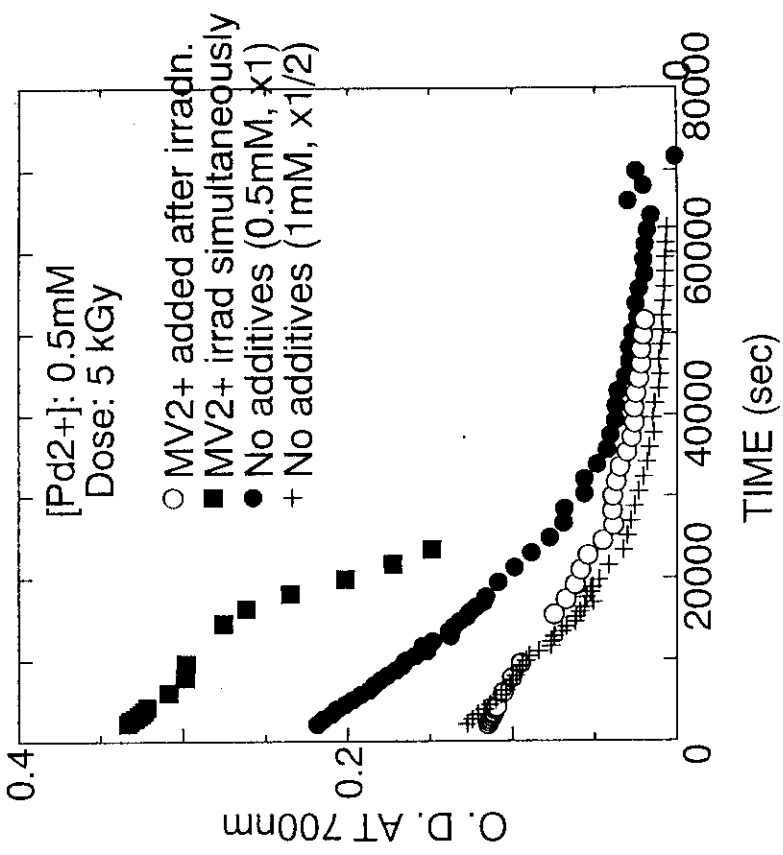


Fig. 22 Turbidity (O. D. at 700 nm) as a function of time (○) after mixing $MV^{2+}$ solution (1 mM, pH: 0.43) with irradiated palladium sulfate solution (1 mM, pH: 0.43, 5 kGy) a few minutes after the irradiation; (■) after irradiation (5 kGy) of [$MV^{2+}$ + palladium sulfate] (0.5 mM + 0.5 mM, pH: 0.43) solution; (●) after irradiation (5 kGy) palladium sulfate solution (0.5 mM; pH: 0.43) ; (+) after irradiation (5 kGy) palladium sulfate solution (1.0 mM; pH: 0.43) , in × 2 scale.

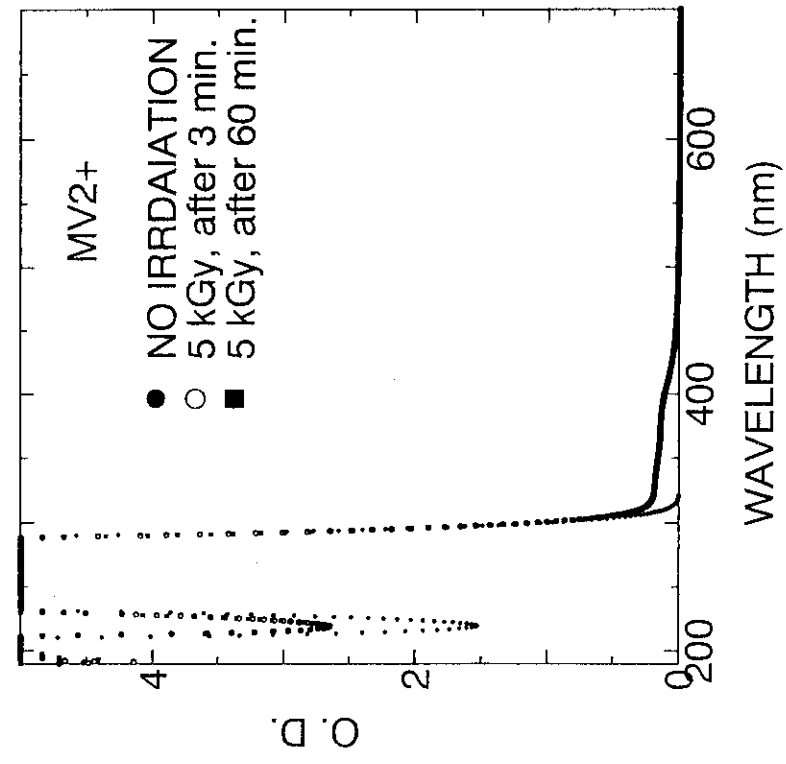


Fig. 21 Change of electronic spectrum of $MV^{2+}$ solution (1 mM, pH: 0.43) after irradiation.

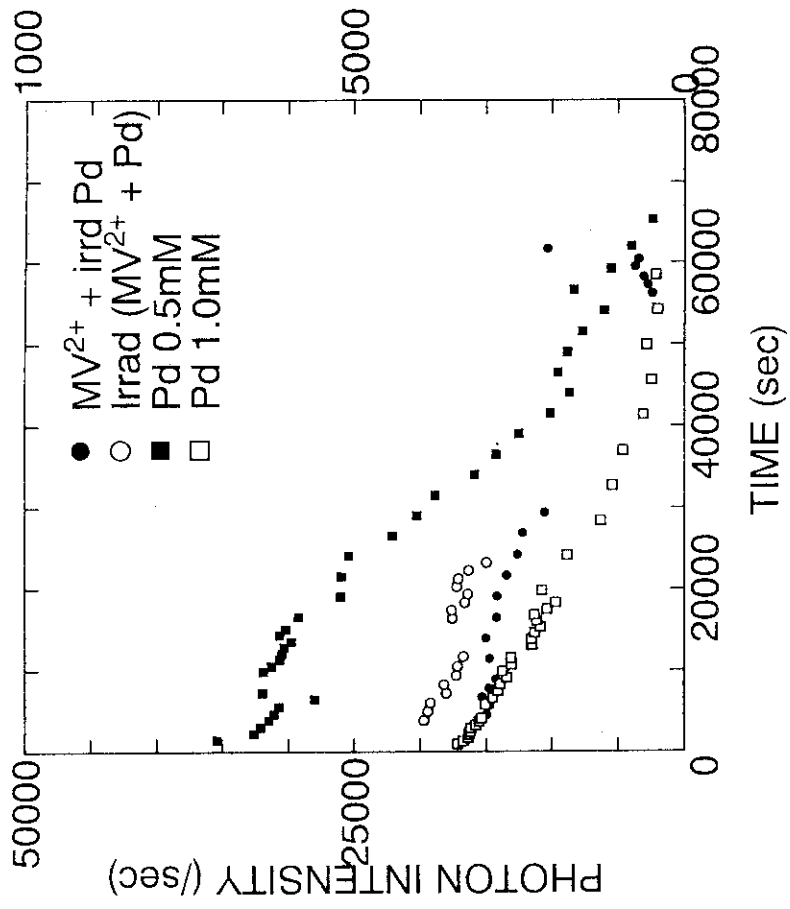


Fig. 24 Photon scattering intensity as a function of time; (●) after mixing $MV^{2+}$ solution (1 mM, pH: 0.43) with irradiated palladium sulfate solution (1 mM, pH: 0.43, 5 kGy) a few minutes after the irradiation; (○) after irradiation (5 kGy) of [$MV^{2+}$ + palladium sulfate] (0.5 mM + 0.5 mM, pH: 0.43) solution; (■) after irradiation (5 kGy) palladium sulfate solution (0.5 mM, pH: 0.43) ; (□) after irradiation (5 kGy) palladium sulfate solution (1.0 mM; pH: 0.43) .

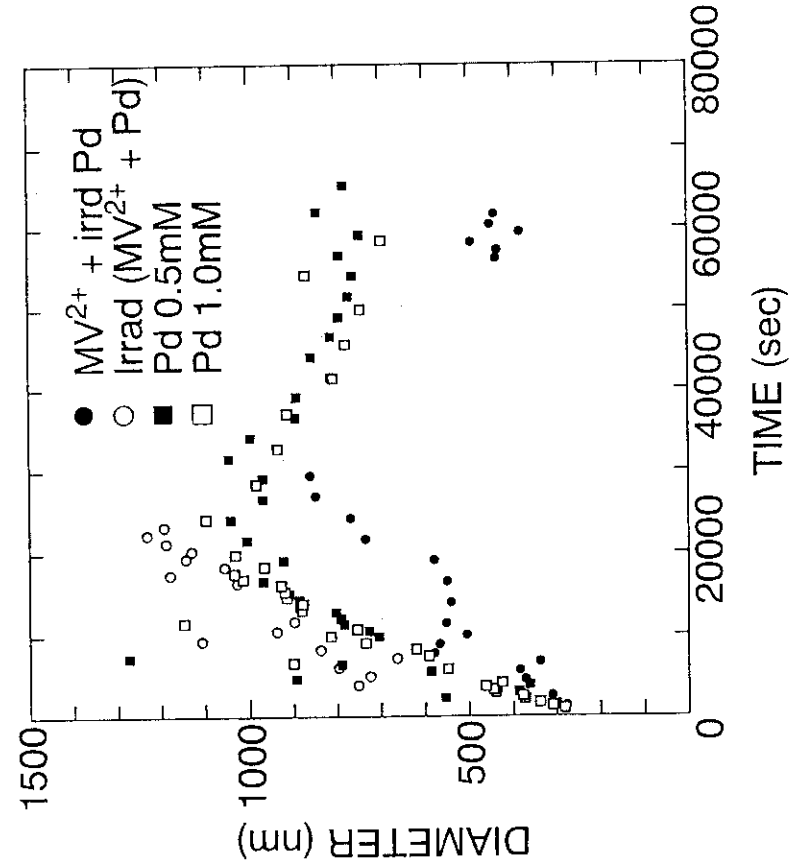


Fig. 23 Average diameter of particles as a function of time; (●) after mixing $MV^{2+}$ solution (1 mM, pH: 0.43) with irradiated palladium sulfate solution (1 mM, pH: 0.43, 5 kGy) a few minutes after the irradiation; (○) after irradiation (5 kGy) of [$MV^{2+}$ + palladium sulfate] (0.5 mM + 0.5 mM, pH: 0.43) solution; (■) after irradiation (5 kGy) palladium sulfate solution (0.5 mM; pH: 0.43) ; (□) after irradiation (5 kGy) palladium sulfate solution (1.0 mM; pH: 0.43) .

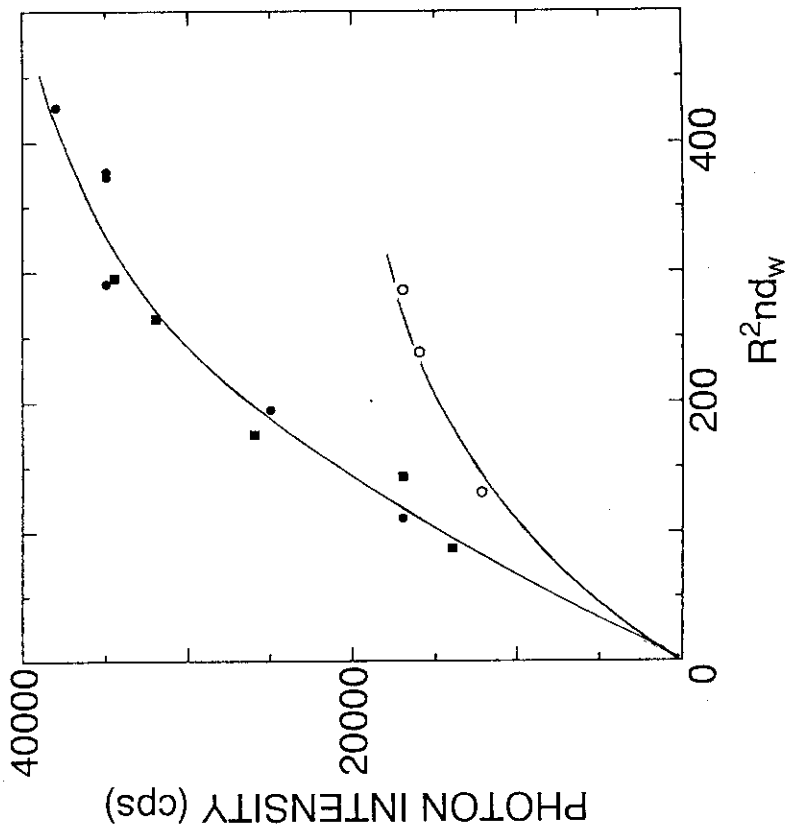


Fig. 25B Photon scattering intensity as a function of $R^2nd_w$; for symbols, see the caption to Fig. 25A.

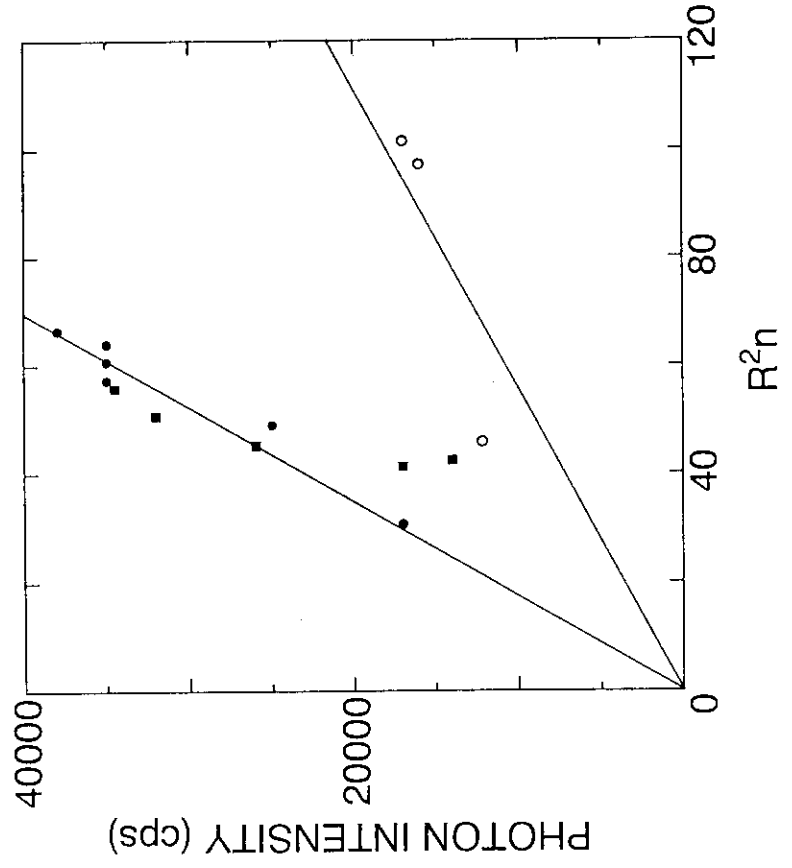


Fig. 25A Photon scattering intensity as a function of $R^2n$; ●■○ data from Table 2 and Fig. 5 (palladium); data from Table 4 and Fig. 13 (palladium); ○ data from Table 6 and Fig. 15 (palladium-silver); the data that were taken 300 sec after the irradiation were used for the calculations and plots.

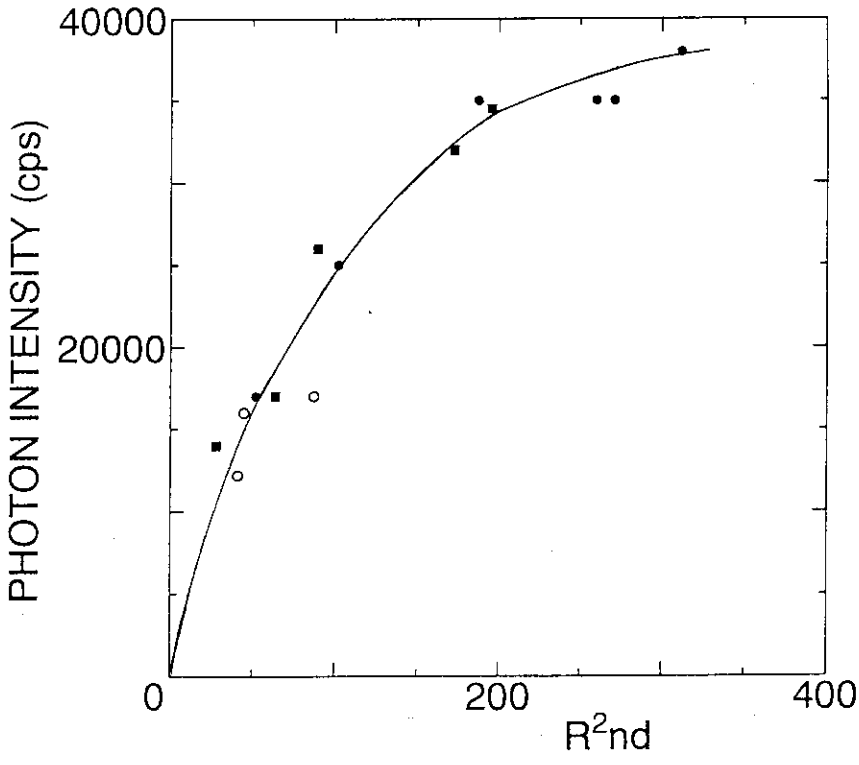


Fig. 25C Photon scattering intensity as a function of $R^2nd$; for symbols, see the caption to Fig. 25A.