JAERI-M
93-248

FORMATION OF FINE PALLADIUM PARTICLES FROM PALLADIUM SULFATE AQUEOUS SOLUTION BY GAMMA-RAY IRRADIATION AS OBSERVED BY ELECTRONIC ABSORPTION SPECTROSCOPY AND DYNAMIC LIGHT SCATTERING

January 1994

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Japan Atomic Energy Research Institute

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編集兼発行　日本原子力研究所
印　　刷　日立高速印刷株式会社

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Formation of Fine Palladium Particles from Palladium Sulfate Aqueous Solution by Gamma-ray Irradiation as Observed by Electronic Absorption Spectroscopy and Dynamic Light Scattering

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(Received December 1, 1993)

To find a way of probing the coagulation of metal particles formed by the irradiation of metallic ion solution without surfactant, palladium sulfate aqueous solution was irradiated with gamma rays (11.2kGy/h, 10kGy) and turbidity change of the solution after irradiation was followed by optical density at 700nm using a UV-visible spectrophotometer. The particle diameter distribution was monitored by dynamic light scattering. The results indicate that the turbidity decreased monotonously, and that there are major peaks in the distributions, one with diameters in the 400-800nm region and the other with diameters in the 1500-2500nm. The density of the particles seems to be smaller than that of bulk palladium metal. Similar experiments were carried out on palladium-silver sulfate solution.

Keywords : Palladium, Particle, Silver, Dynamic Light Scattering, Electronic Spectra, γ-ray , Irradiation

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* Argonne National Laboratory

電子スペクトルおよび動的光散乱法を用いた硫酸パラジウム水溶液のγ線照射によるパラジウム微粒子生成の観測

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

（1993年12月1日受理）

安定剤が存在しない金属イオン水溶液のγ線照射により生成する金属微粒子の凝集機構を調べる方法を見出すために，硫酸パラジウムを窒素飽和した後，γ線照射（11.2kGy／h，10kGy）を行った。照射後の溶液の濁度変化を可視紫外分光光度計を用いて700nmにおける吸光度により調べ，また生成した固体微粒子の粒子径分布の時間的変化を動的光散乱粒子径アナライザーを用いて研究した。濁度は単調に減少すること，また生成した微粒子の粒子径分布は，400－800nmと1500－2500nmにピークを持つものであることがわかった。得られた粒子の密度は，バルク金属の密度よりも小さいものであることが考えられる。同様の研究を硫酸パラジウム－硫酸銀水溶液についても行った。

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1. INTRODUCTION

Past studies in other laboratories have shown that the radiolysis of metal ions will form metallic clusters, colloids, and finally macroscopic particles.

In research previously done at Osaka Laboratory for Radiation Chemistry [1], it was shown that similar reactions occur in pH 1.43 solution of palladium sulfate and mixtures of palladium sulfate and silver sulfate, but not for silver sulfate solution alone. It was also shown that stirring of palladium sulfate solutions after irradiation accelerated the precipitation reactions.

The present studies were carried out to find a way of probing the coagulation of metal particles formed by the irradiation of metallic solutions using UV-visible absorption spectroscopy and dynamic light scattering (DLS). It is hoped that if the formation mechanisms are understood, it will be possible to control the growth processes. Previous workers in the field have used surfactants, either poly-anions or poly-amines, to control growth. Because the goal of this research program is the development of catalysts, the possible contamination of the final products with the surfactant makes the use of such techniques undesirable. In addition, organic feedstocks would be expected to remove the surfactants, and thus the stabilization of the small colloidal particles could not be supported in use.

A computer survey was made of the literature to find references to the creation of particles using radiation conditions [see Appendix 1]. Only one reference was found to bimetallic particle creation, and that paper used photolytic techniques [ref. 12 in Appendix 1]. There has been little work done on doubly charged species. Recently there was the first report of work where palladium particles were formed [ref 8 in Appendix 1]; however that work was primarily concerned with the early stages of solid formation. There does not appear to be any consensus on the mechanism that creates small metallic particles from doubly charged ions.

2. EXPERIMENTAL

A Pyrex glass tube containing 15 ml aqueous solution of 1 mM of palladium sulphate or 0.5 mM palladium sulphate and 0.51 mM silver sulphate both at pH=1.43 was sealed with a rubber septum. The solution was degassed by bubbling the

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solution with nitrogen, which was put into the vessel by a needle through the septum. Samples thus made were irradiated with a dose rate of 10kGy using a cobalt-60 gamma radiation source with a dose rate of 11.2kGy/h. Irradiation conditions are summarized in Table 1.

A technique was devised to transfer the irradiated samples to measurement vessels for the dynamic light scattering (DLS) apparatus and the visible-UV spectrophotometer without exposing them to air. This was done by putting the sample tube and cells into a polyethylene bag filled with nitrogen. The septum was removed and the solution was transferred to the measurement vessels in the bag.

The light transmission was measured using a Shimadzu 3010 UV-visible spectrophotometer. Particle size distribution was measured on an Ohtsuka 600 DLS unit equipped with a He-Ne laser source.

Previously, time-dependent data had been taken from plots made by the visible-UV spectrometer. Using an option of the program controlling the visible-UV spectrophotometer and a Basic program, data were transferred to a plotting program "Igor" on a Macintosh or were transferred to the OASYS system for plotting. This made it possible to make use of all the data gathered and to do so more conveniently than reading the data of the hard copy.

3. RESULTS AND DISCUSSION

3.1. Palladium system

The absorbance of the palladium system was plotted as a function of time in Fig. 1a and 1b (extended time scale), along with the plots obtained in the past experiments[1], where irradiated solution was exposed to air for short time (a minute or so) when the solution was transferred to a cuvette for visible-UV spectrophotometry. The plots obtained in this study (denoted as p27, ・and p28, △) agree well each other, but are 17 % and 11%, respectively, higher than the corresponding former experiment (p9, +). The higher values may indicate that there was some contamination with oxygen in the earlier experiments. The absorption obtained in a previous experiment where AOT (Aerosol OT; di-2-ethyl hexyl sodium sulfosuccinate, $C_{20}H_{37}O_7Na$) was added after the irradiation (plotted with □, p23) decayed rapidly at earlier period, and the expected effect of AOT to protect particles seems only to occur at the later stage. The absorption obtained under continuous agitation decayed quickly compared to the other three experiments. The absorbance was plotted as a function of time in Fig. 2 along with an exponential fit. The absorbance decays with approximately

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an exponential form with a half life of about 6400 seconds. The initial 1200 seconds is not fit well by the exponential, but the remainder is. This wide time distribution shows that there is considerable diversity in the size of the particles. This result is confirmed by the DLS results as shown in Figs. 3, 4a, 4b, and 5, where fraction was plotted as a function of particle size in nm for p27, p28 at earlier period, p28 at later period, and p29, respectively. Different symbols in the figures indicate distributions taken at time t(in minutes) after the completion of the irradiation. The distribution curve changes with time considerably, e. g., × and □ in Fig. 3, showing that small particles combine each other to form large particles which are subsequently removed from the solution by faster precipitation rate than those of small particles. The results of these DLS experiments show that in the first few hours, there are two major peaks in the distributions, one with diameters in the 400-800nm region and the other with diameters in the 1500-2500nm. The particles do not appear to grow but last a considerable time. There seems to be a certain shrinking after growth.

The fact that the particles do not precipitate out quickly shows that the particles do not have the same density as solid palladium. If the density were that of the solid palladium, time required to move one cm decreases with increasing diameter of the particle as shown by the curve calculated by Stokes' law using density of solid palladium (12.0 g/cm^3) in Fig. 6. Therefore, the particles in the 1000-2000nm region would settle in a few minutes. The results of DLS experiments suggest that the particles in 1000-2000nm region still exist a few hours after irradiation (Fig. 3, 4a, 4b, and 5). If one uses the Stokes' law for settling velocity of these particles, one must use a much lower density for the material than that of solid palladium. This is consistent with a porous particle.

After all materials were settled, one can re-stir the solution and observe the change of absorption with time. The results are shown in Fig. 7a and 7b (extended time scale up to 2000 sec) along with the original settling curve. The change in absorption due to settling of the solids formed by the irradiation show a sharp decrease at approximately 10-15min. This is suggestive of a relatively mono-disperse system. Decays of photon counting and absorption were plotted on the same time scale in Fig. 8. Different slopes observed for these plots are not understood at present. There is a linear relation between photon count and absorption as shown in Fig. 9.

An explanation of the results mentioned above can be made if small clusters of small colloidal particles are formed. These can coagulate; however it is

likely that if two clusters come together, they will separate. This is because they will join much as beads and will not form a larger sphere. If an additional particle joins the pair, it may join on the end; alternatively, it could join so that it interacts with both particles. This latter addition will then strengthen the combination. This type of mechanism would suggest that there might be small particles or combinations of several small particles, but that the combination of only a few particles would not be stable- several small particles have to join for the larger particle to be stable.

The results also suggest that the clustering of the small particles might be a dynamic process - if there were two different sizes and these two sizes did not change, one would expect a two-step settling process. Instead the settling process is constantly changing as the size of the particles changes.

Several questions remain to be answered concerning the palladium particle system. 1) One would like to have a good idea of the shape of the particles. Because the particles change as a function of time, the shape needs to be measured on the time scale of that change -- 20 - 30 minutes. Possibly DLS experiment at different angles could be useful. The density of the particles is of interest because it will be an idea of the porosity of the particles. It may be possible to learn this from the settling times and the particle diameters. 3) for catalytic activity, surface area may be very important. Possibly this area can be determined by gas adsorption experiments. 4) The charge on the particles as a function of time will help explain reactivity and coagulation. A. Henglein [ref. 8 in Appendix 1] has shown that methyl viologen will react with clusters that are positively charged. One can do an irradiation and separate the sample into several tubes. Methyl viologen could be added to the different tubes at different times and the methyl viologen cation measured. This would give the oxidising power of the particles. 5) Can the growth of the system be simulated as a function of time? It may be possible to simulate using differential equations; however we expect that the growth process may well be fractal. It may be possible to derive a fractal dimension for the particle growth.

3.2. Palladium-silver system

The studies of the silver-palladium system are less advanced. As shown in Fig. 10, all three experiments are in concord in that the optical absorption increased with time at earlier period up to 5000 sec and then decreased with time. However, two of the three experiments (indicated as pal2, • and pal4, □) show a sharp drop in the optical absorption as a function of time; this

result is consistent with the particles all being about the same size, since the time required to go out of the optical path region in the cuvette is the same for the particles of the same size according to Stokes' law. This indeed appears to be shown by the size distribution obtained from the DLS experiments, which are shown in Fig. 11a, 11b (integrated and normalized to 100%), 12, and 13. The third experiment (pa13, + in Fig. 10) shows a broader distribution in settling times, and this is reflected in the distribution of particle sizes as shown in the table 2, which summarizes the distribution curves with time after irradiation. These results may depend critically on sample purity.

It is shown in Fig. 11b that particle size continuously shifted to larger size with time with two exceptions (■ and ×).

An example of DLS data print out and conditions of the DLS analysis are shown in Fig. 14.

3.3 A model for particle growth

A model for particle growth for palladium particles was formulated and the equations were solved using the program "Mathematica". The basic chemical assumptions of the model are outlined in the following reaction mechanism.

Pd(+2) + 2(electron) -----> (1/30) Pd(solid)
Pd(solid) + Pd(solid) -----> Pd(solid dimer)
Pd(solid) + Pd(solid dimer) -----> Pd(solid trimer)
Pd(solid) + Pd(solid trimer) -----> Pd(solid tetramer)
Pd(solid dimer) + Pd(solid dimer) -----> Pd(solid tetramer)
Pd(solid trimer) -----> Pd(trimer precipitated)
Pd(solid tetramer) -----> Pd(tetramer precipitated)

Note that in this mechanism the reaction of Pd(2+) with the electron is in competition with other electron scavengers in the solution. The amount of the electron that reacts with the Pd(2+) is described using a Stern-Vollmer equation. In addition, it is assumed that there is coagulation to form particles initially of the order of 30 palladium atoms. The rate of the precipitation reactions will be due to the size and density of the particles.

The setup and commands for the solution of these equations are given in Appendix 2 and the concentrations are plotted in the upper panel of Figure 15. The lower panel displays the difference between the initial palladium ions and the total amount of palladium in the calculation. The small fluctuations around zero demonstrate that the solution of the equations was sufficiently accurate.

The results of these calculation show a steady progression to large particle sizes - a result that is inconsistent with the experimental results given above. It has been suggested above that these results should be simulated using a non-continuum approach, and that possibly a fractal description could be derived. These calculations are consistent with this premise; however, there may be other alternatives. These must be explored.

4. CONCLUSIONS

Irradiation of gamma rays on dearated palladium sulfate aqueous solution without any surfactant resulted in formation of small particles. DLS measurements on the irradiated solution allowed us to determine that the particles size distribution in the solution showed two peaks at 400- 800nm and 1500-2500nm. Time-dependent DLS measurement indicated that the distribution changed with time suggesting that there exist some combined processes of coagulation of the small particles and sedimentation of the coagulated aggregates. The fact that particles of large size still exist in the solution for a few hours that is longer than sedimentation time than that expected for particles of the same density as that of bulk palladium. Further studies will be necessary to obtain reproducible results on palladium-silver system. The time-dependent DLS measurement combined with optical density measurement seems to provide effective probing technique for study of the formation and growth mechanism of metal atoms in the solution.

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Table 1 Dose and concentration of metal after irradiation

Run	dose(kGy)	[Pd2+](mM)	[Ag+](mM)
p27	11.16	0.56	-
p28	11.23	0.40	-
p29	11.23	0.43	-
pa12	11.23	0.40	0.45
pa13	8.98	0.40	0.42
pa14	11.66	0.42	0.38

Table 2 Particle diameters in nm at which the number of particles becomes maximum in Figs. 11a, 12, and 13

Run number / Waiting time (min) pa12/pa14/pa13	pa12		pa14		pa13	
23/25/27	+	750	+	400	+	450
50/51/49	×	850	×	600	×	140
77/78/74a	□	1100	□	550	▲	140,170,220,1200
103/104/99	△	120,160,800S	△	1500	□	180, 1100
133/ - /124	○	1300			△	180
158/143/150	■	400,1600W	○	750	○	950B
187/177/176	▲	650,1500	■	140	■	220,900
215/211/204	◆	1800	▲	900,4000	▲	140,180,220,1200
- / - /234					◆	1200S,1700,2400
312/276/294	●	1300	◆	1000,3000	●	1300B
- / - / 367					×	2000

S: strong B: broad W: week -:no measurement

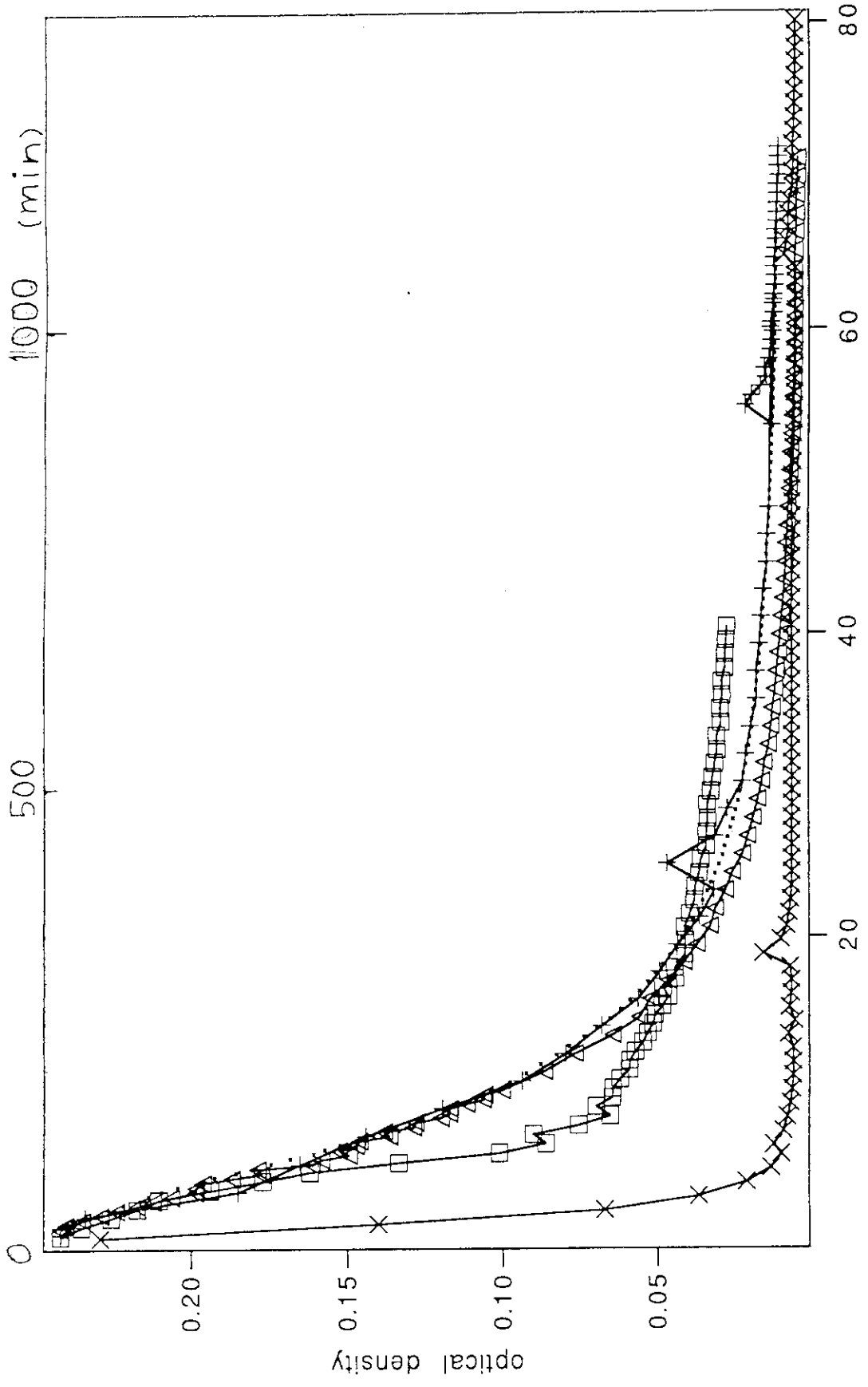


Fig. 1a. Optical density at 700nm as a function of time; time range from 0 to 80000 sec. Solution: 1 mM palladium sulphate aqueous solution; (·) p27; (+) p9 (Fig. 8a and ○ in Fig. 18[1]) times 1.17, (×) p11, (△) in Fig. 18[1]; (△) p28 times 1.06; (□) p23 (AOT added after irradiation) times 1.04.

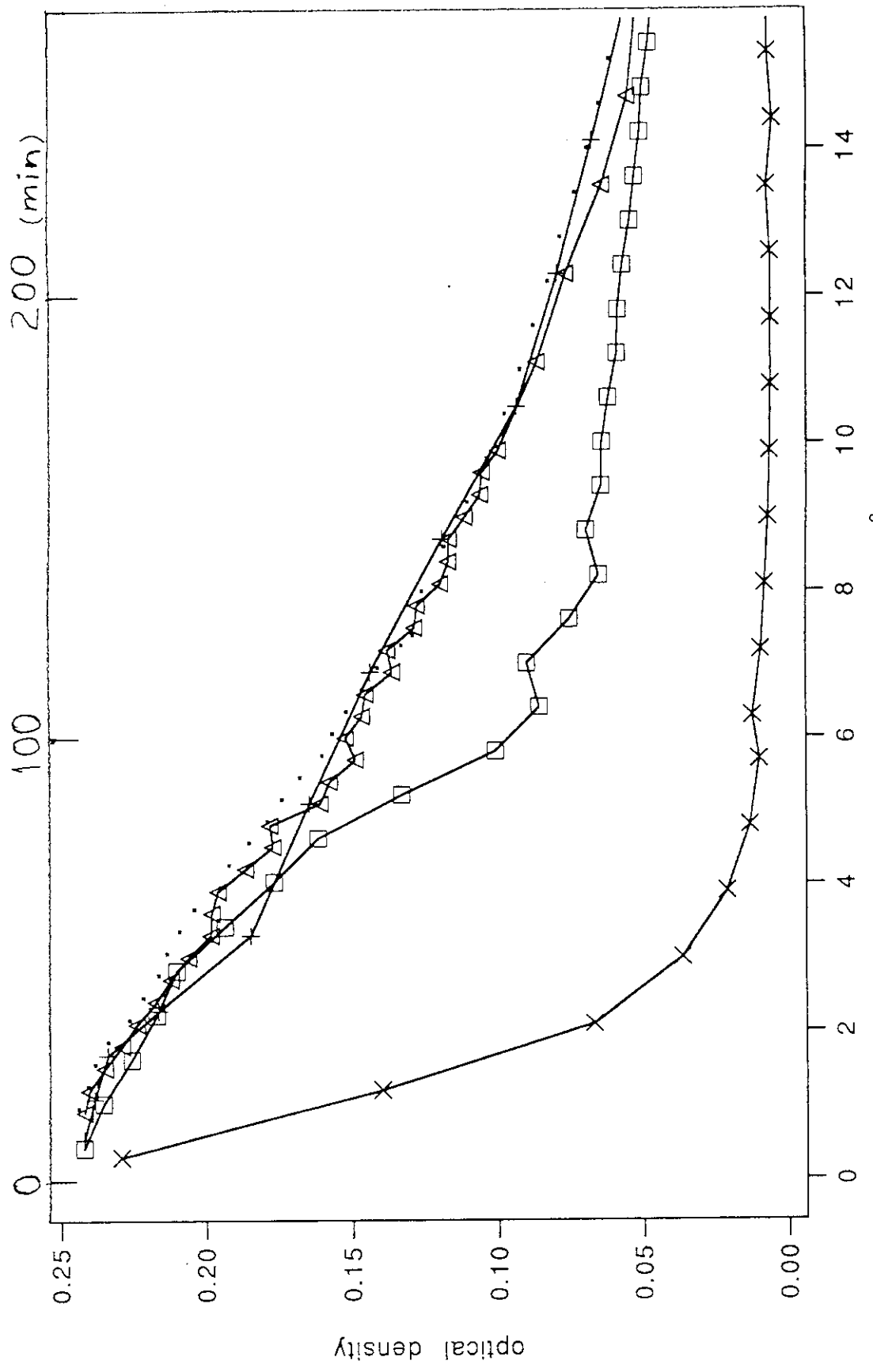


Fig. 1b. Optical density at 700nm as a function of time; time range from 0 to 15000 sec; 1 mM palladium sulphate aqueous solution; Symbols are the same as in Fig. 1a.

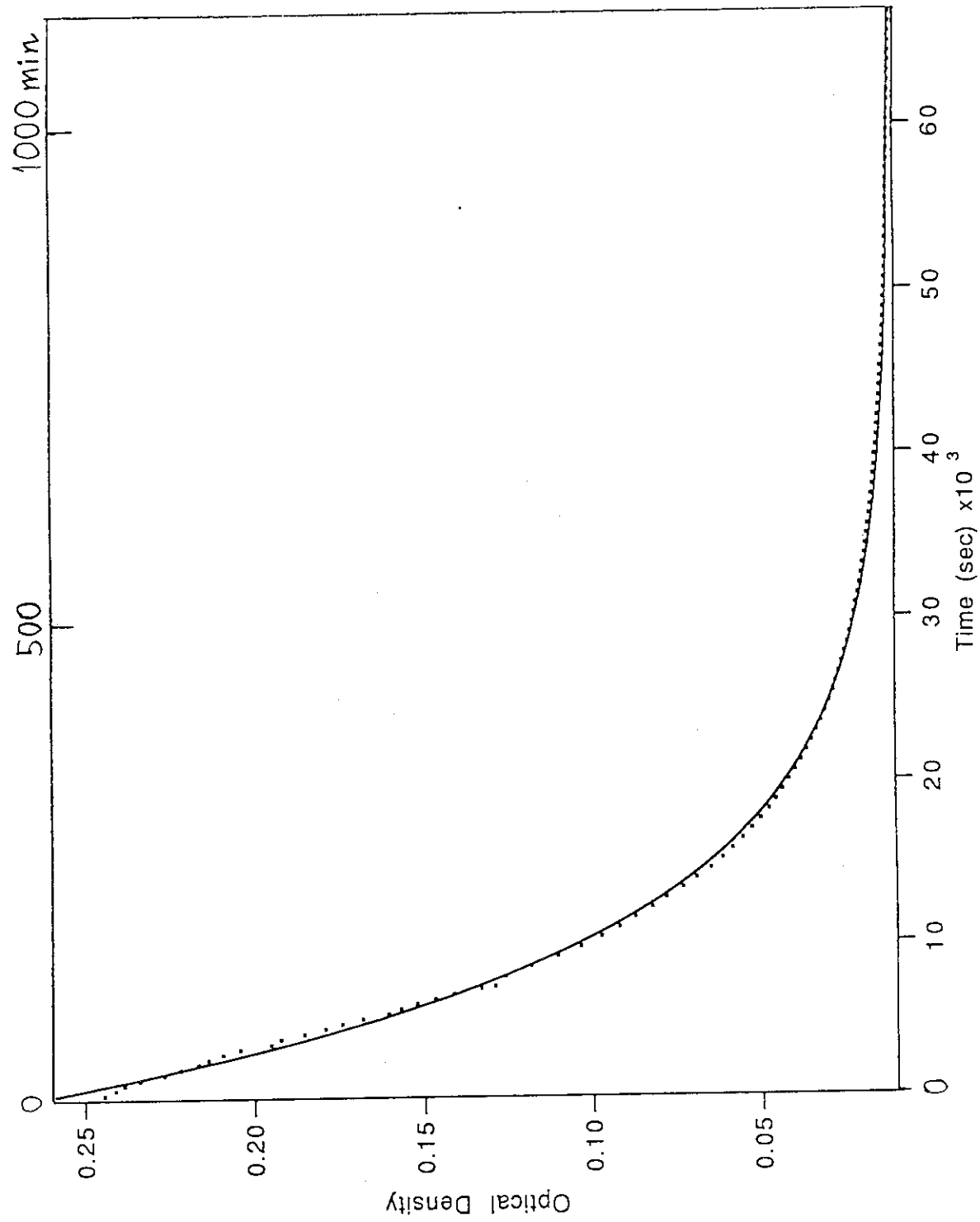


Fig. 2. Optical density at 700nm as a function of time with exponential fit; time range from 0 to 15000 sec; (·) p28, —— exponential.

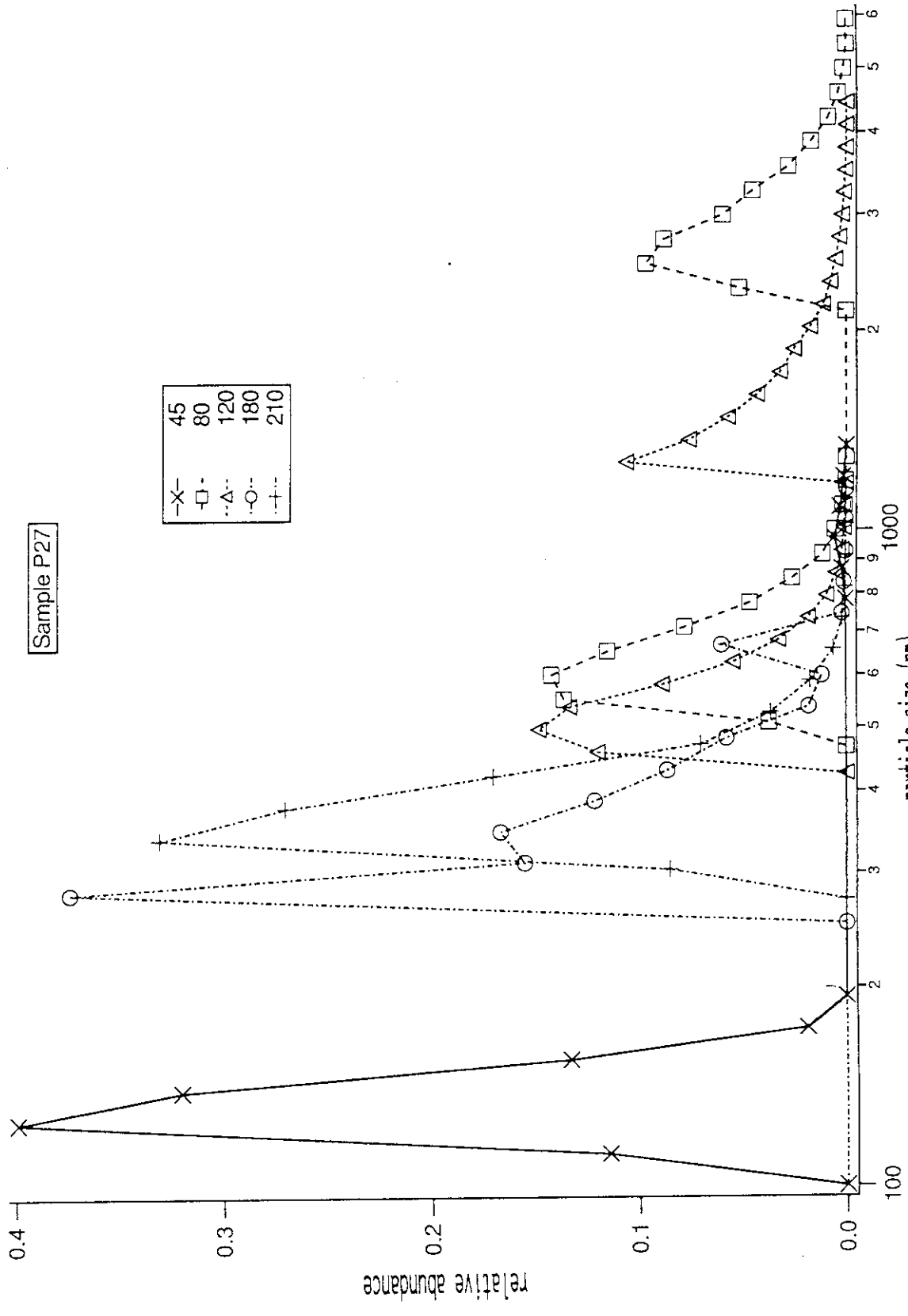


Fig. 3. Distribution of particle size obtained by DLS method measured at different waiting times after irradiation; numerals after symbols in the figure denote waiting time in minute after irradiation. Solution: 1 mM palladium sulphate aqueous solution (p27).

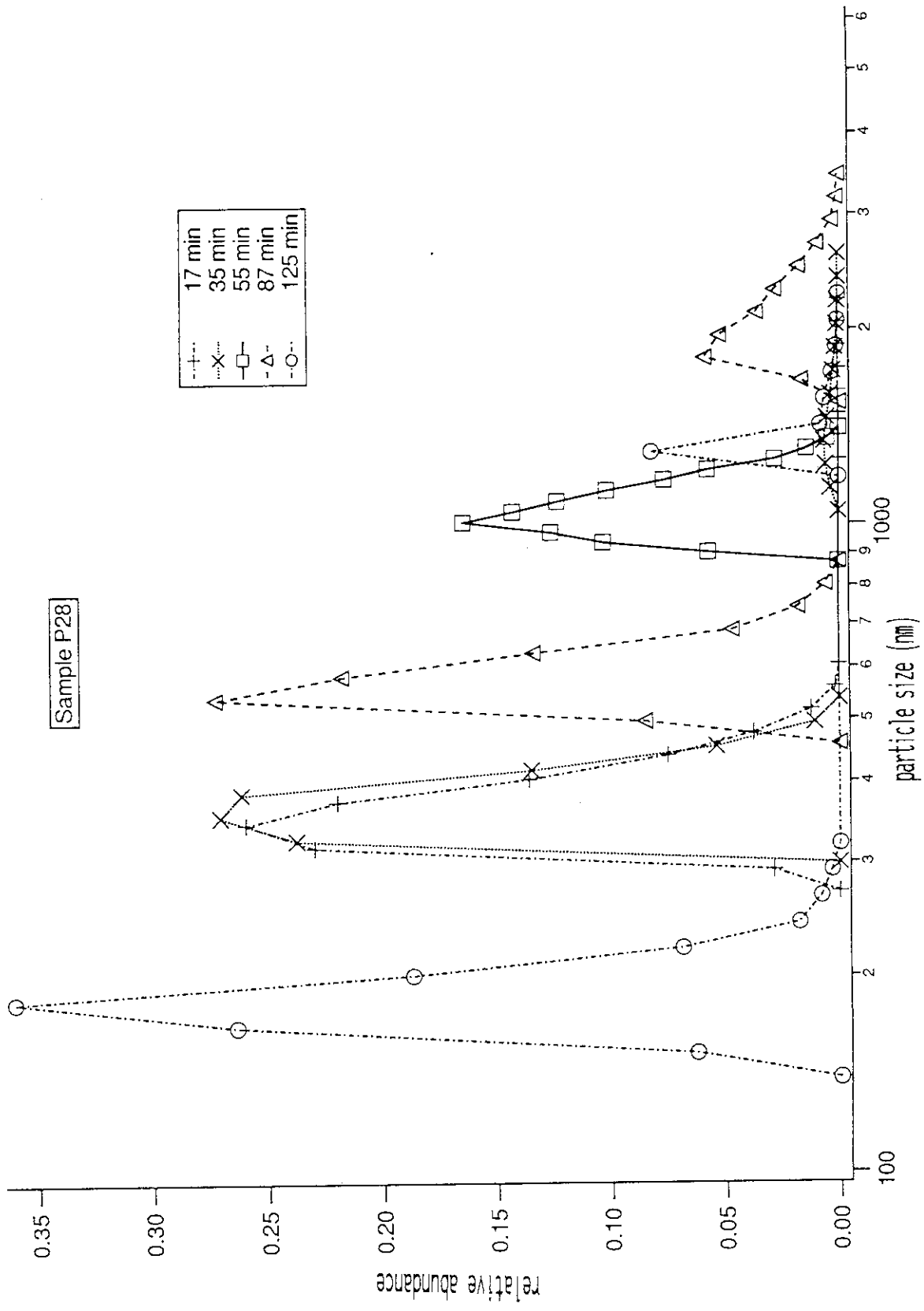


Fig. 4a. Distribution of particle size obtained by DLS method measured at different waiting times after irradiation; numerals after symbols in the figure denote time in minute after irradiation (the same as in Fig. 3, to show reproducibility of the experiment).

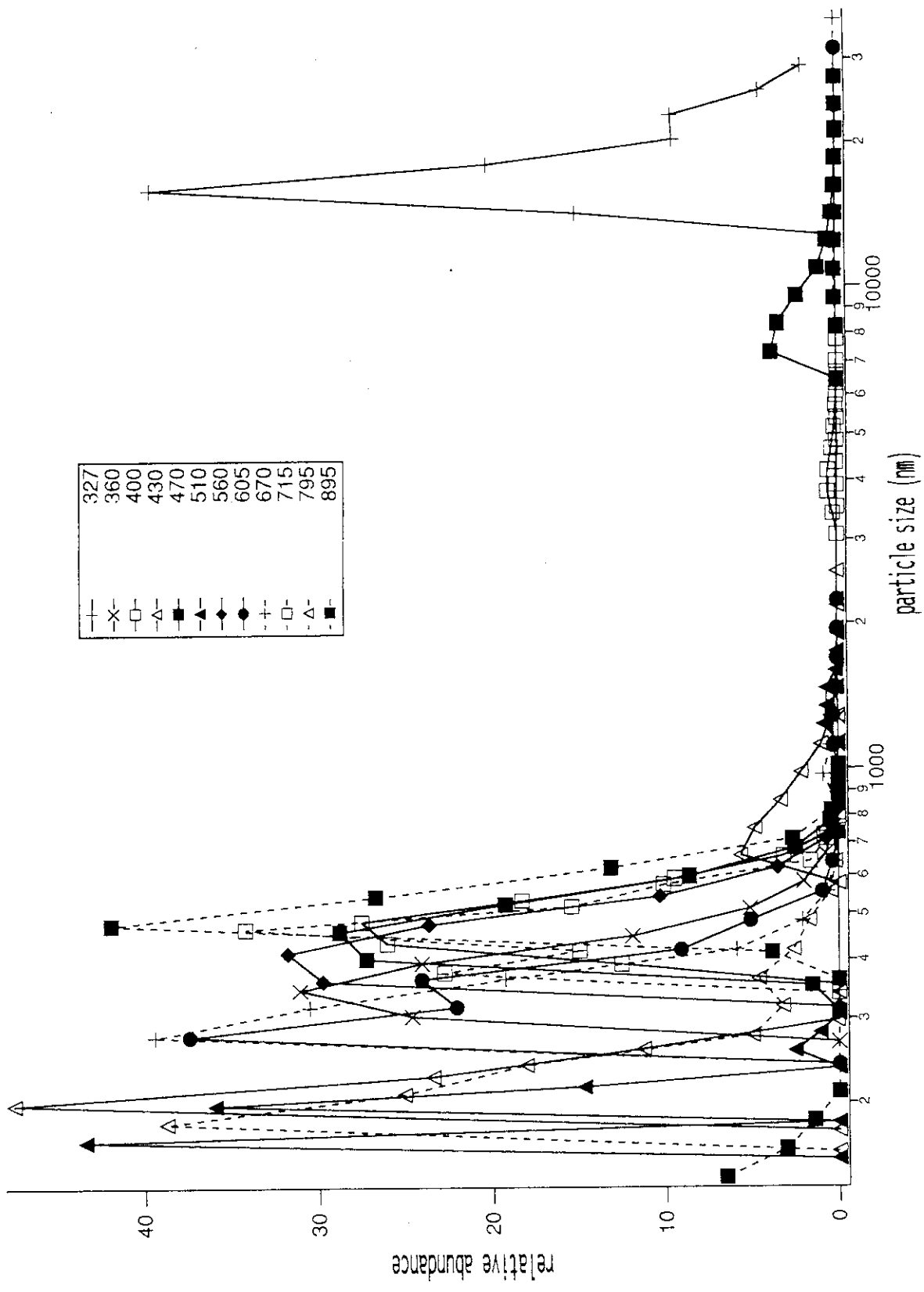


Fig. 4b. Distribution of particle size obtained by DLS method measured at different waiting times after irradiation; numerals after symbols in the figure denote time in minute after irradiation (continuation from Fig. 4a for the runs after 327 min).

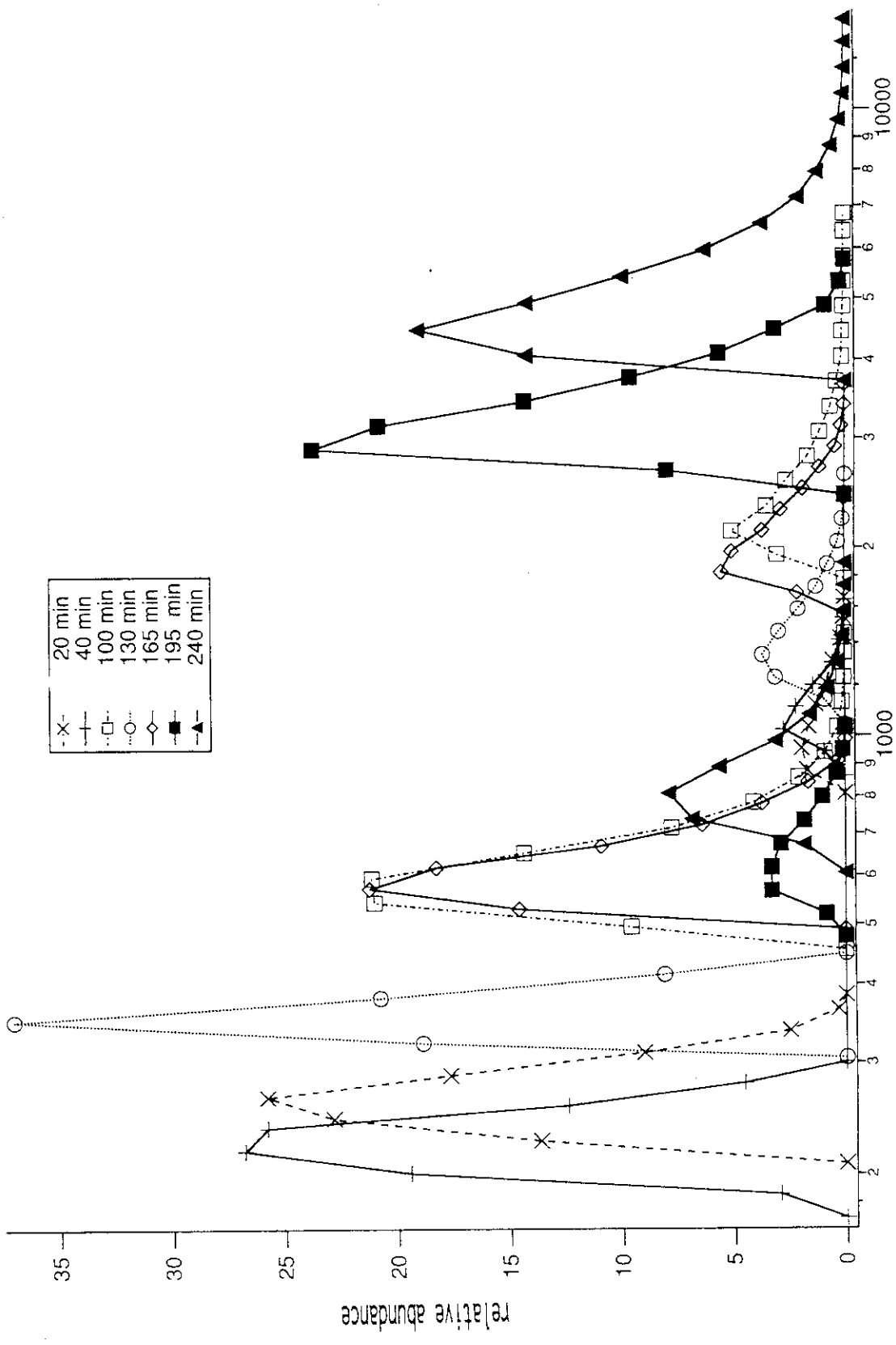


Fig. 5. Distribution of particle size obtained by DLS method measured at different waiting times after irradiation; numerals after symbols in the figure denote time in minute after irradiation (the same as in Fig. 3 and 4, to show reproducibility of the experiment).

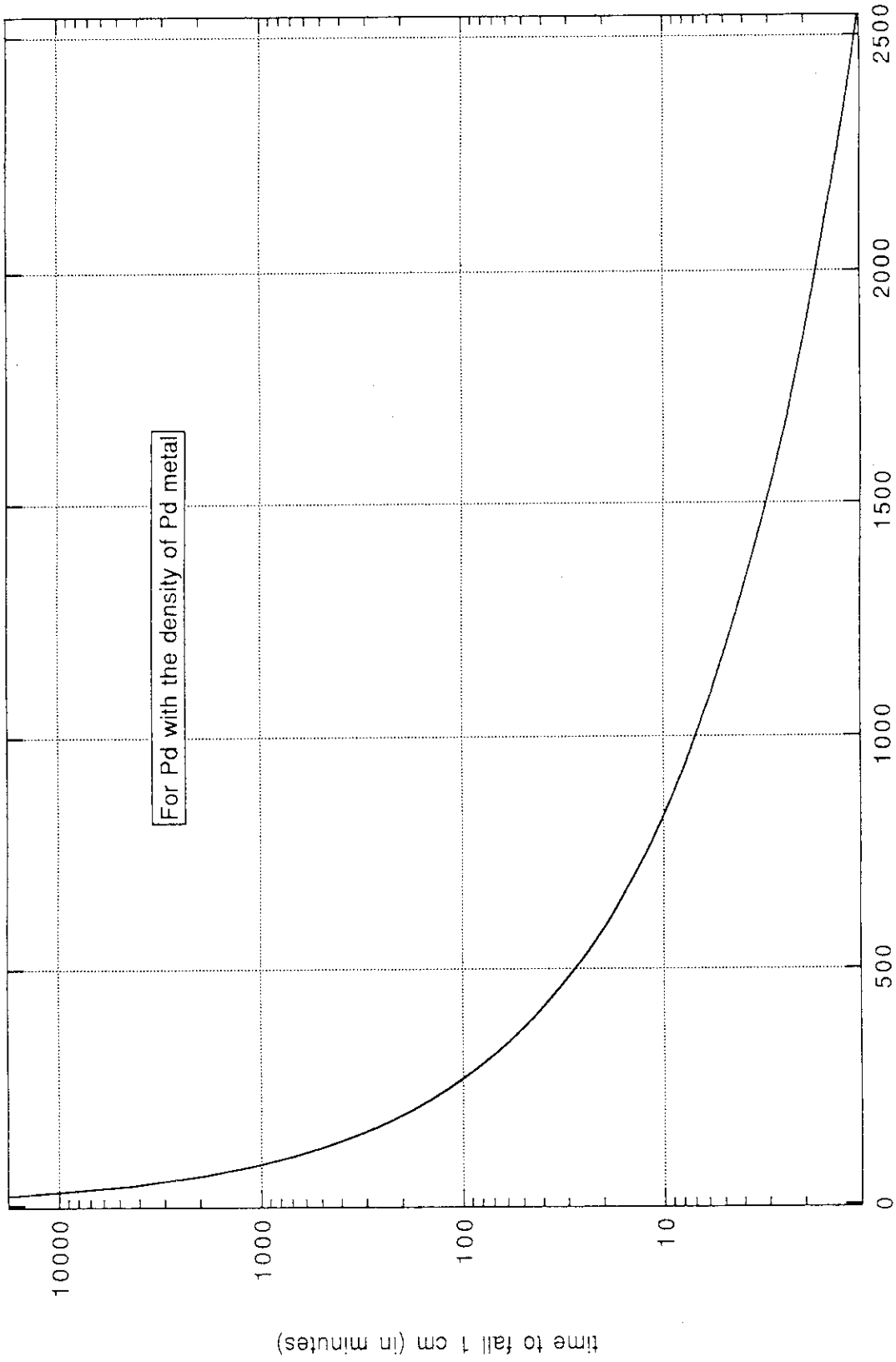


Fig. 6. Calculated time to fall one cm distance for a particle as a function of diameter of the particle assuming the density of the particle is that of palladium metal.

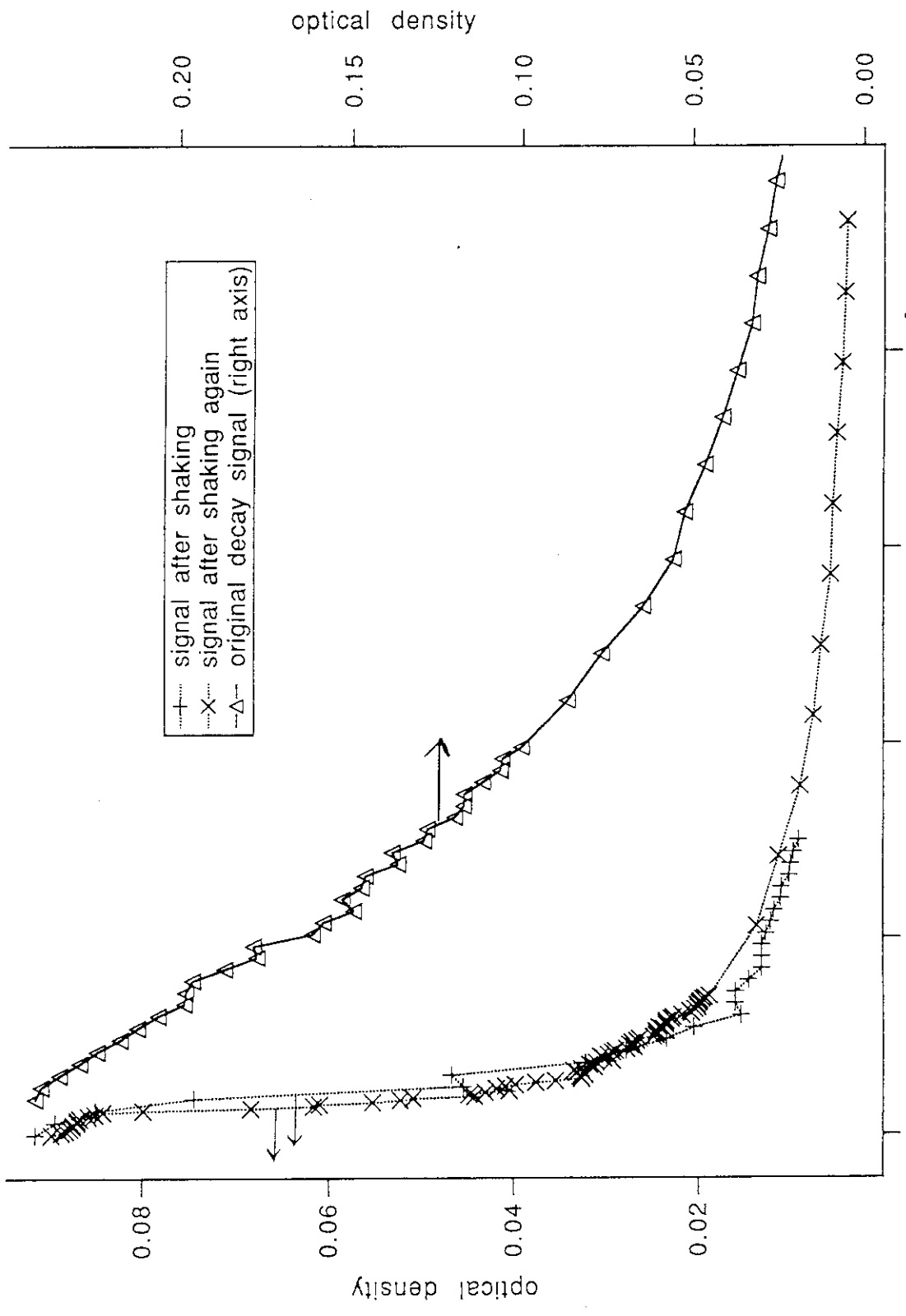


Fig. 7a. Optical density at 700nm as a function of time; time range from 0 to 2500 sec; Original decay curve and decay curves after re-shake of the sample after settling of the suspended particles. Decay curves of the two successive re-shake experiments give reproducible curves. Solution: 1 mM palladium sulphate aqueous solution.

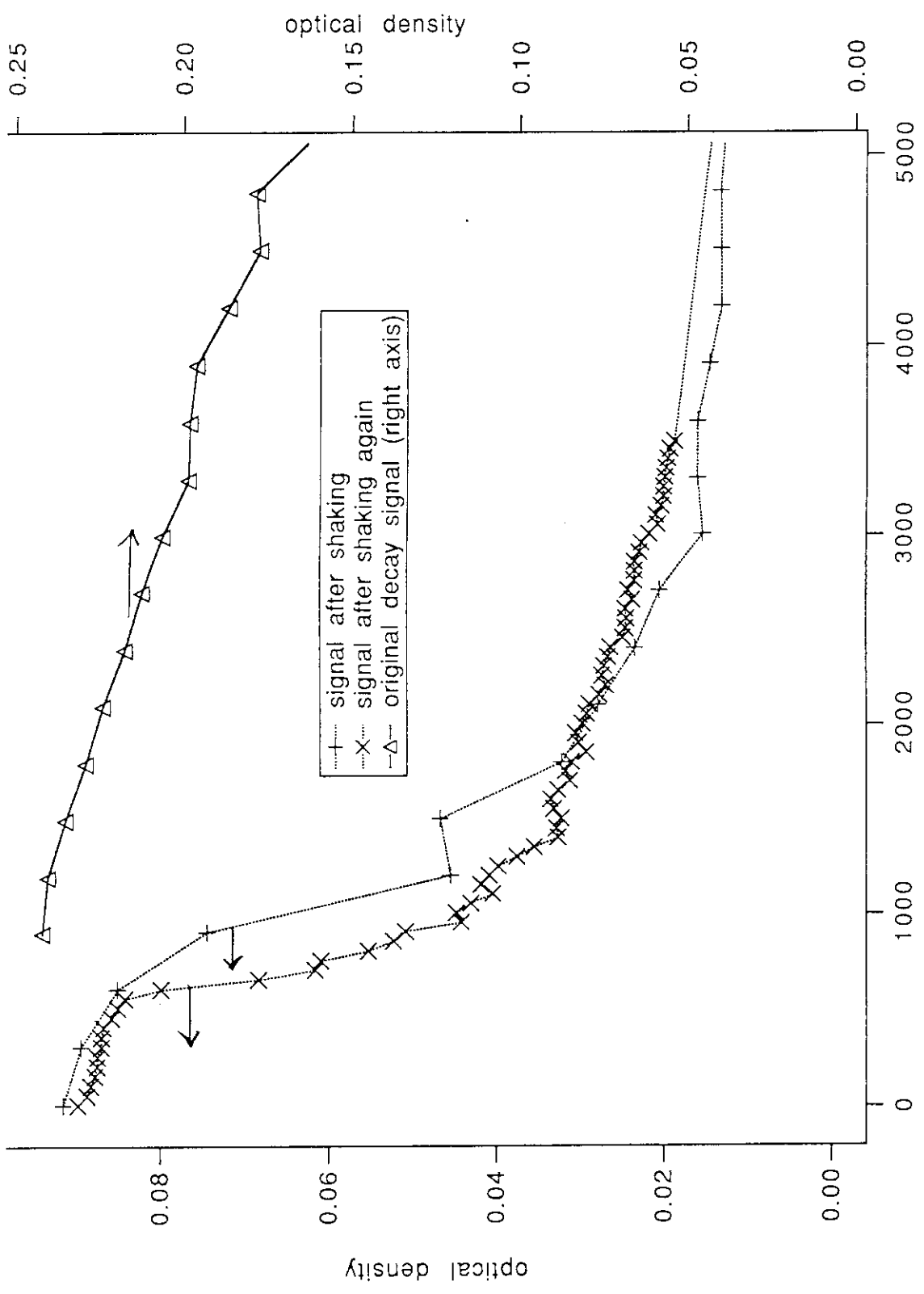


Fig. 7b. Optical density at 700nm as a function of time, showing earlier period of the curves in Fig. 7a. Solution: 1 mM palladium sulphate aqueous solution.

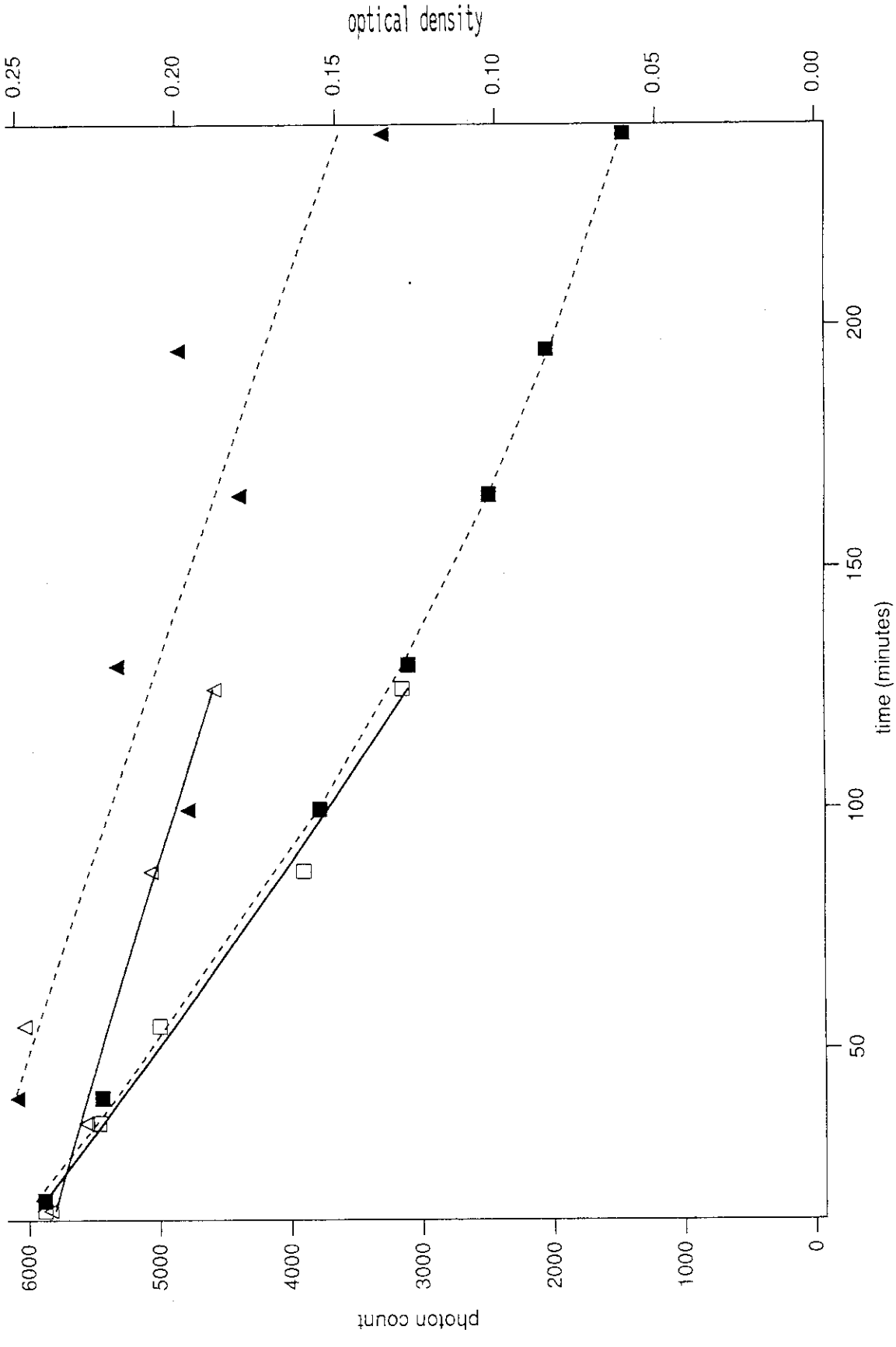


Fig. 8. Comparison of the decay curves for light scattering intensity and optical density at 700nm; scattering photon count; (△) p28, (▲) p29; O. D. at 700nm: (□) p28, (■) p29.

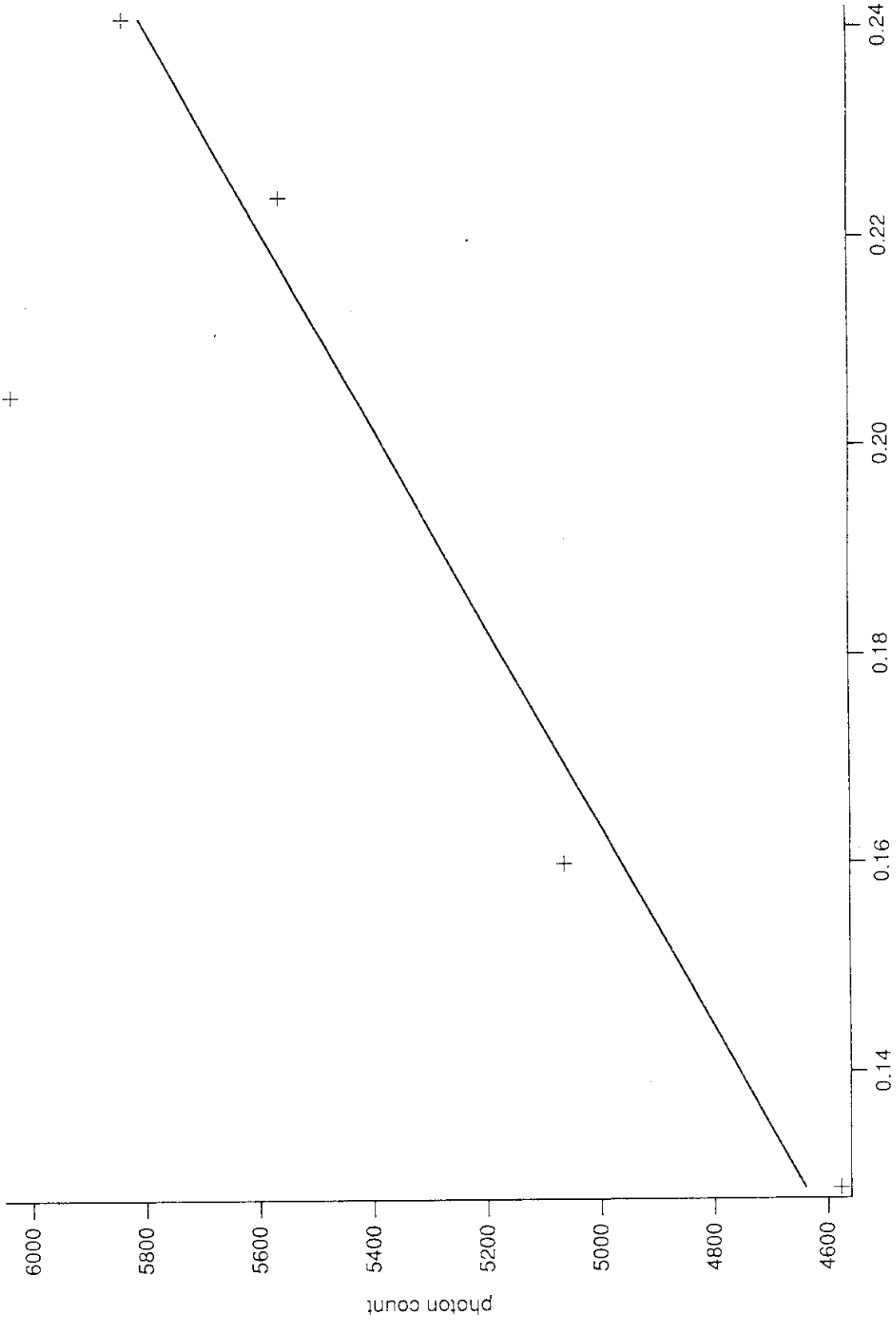


Fig. 9. Plot of scattering intensity as a function of optical density. Solution: 1 mM palladium sulphate aqueous solution (p28, △ and □ in Fig. 8).

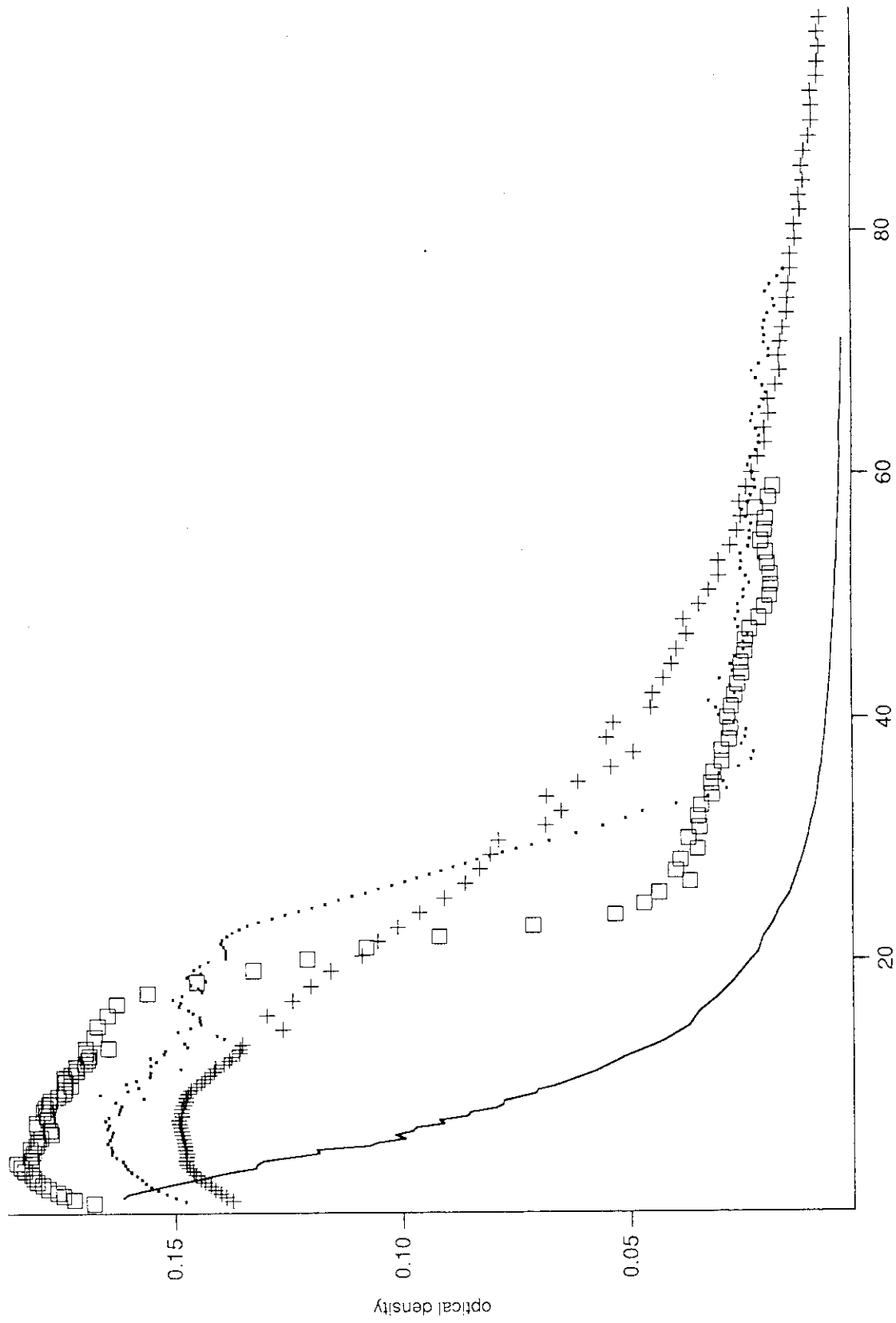


Fig. 10. Optical density at 700nm as a function of time; time range from 0 to 80000 sec. Solution: 0.5 mM palladium sulphate-0.5mM silver sulphate aqueous solution; (·) pal2, (+) pal3, (□) pal4. Curve (——) obtained for Pd alone (p28, times 2/3) is shown for comparison.

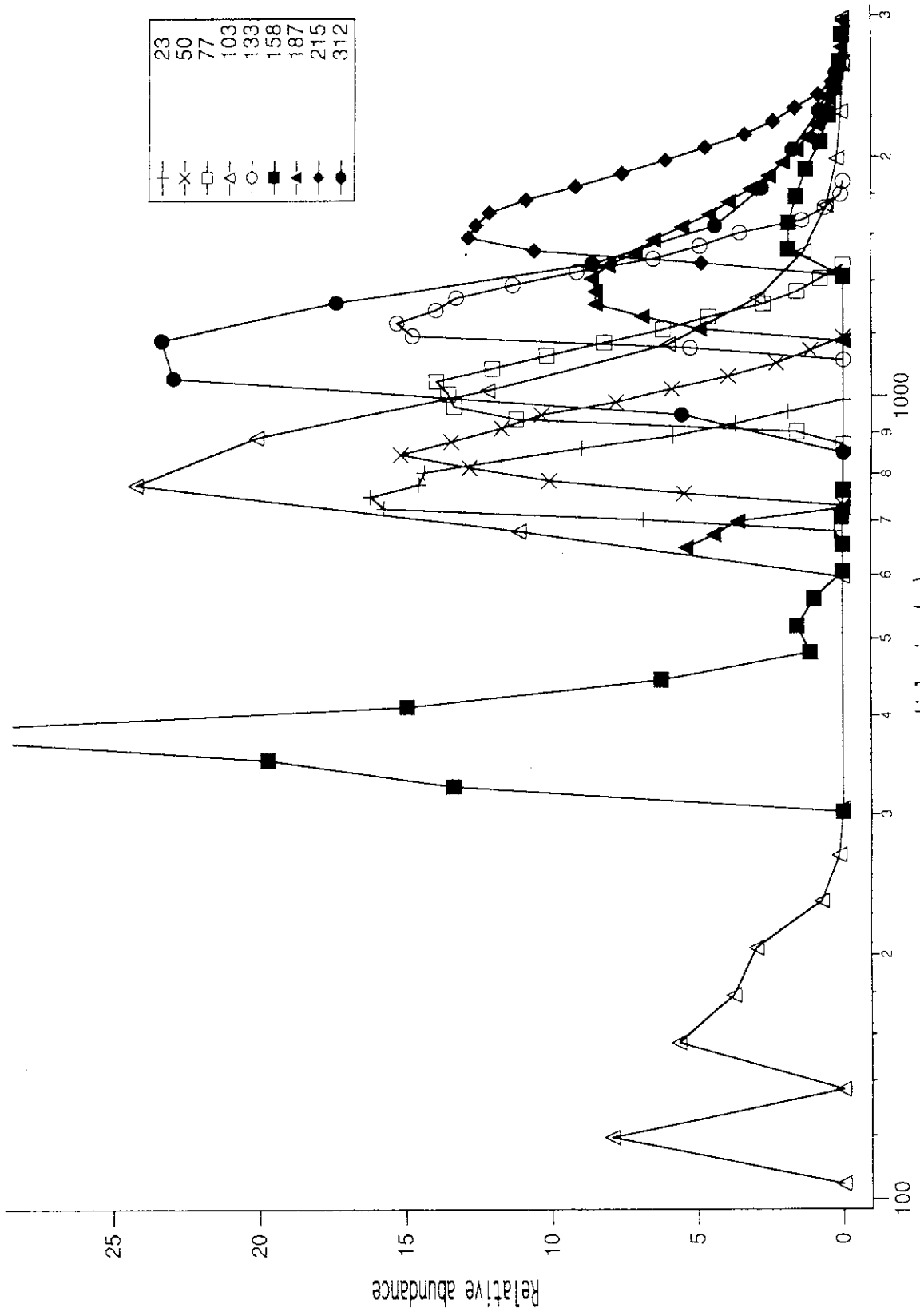


Fig. 11a. Distribution of particle size obtained by DLS method measured at different waiting times after irradiation; numerals after symbols in the figure denote waiting time in minute after irradiation. Solution: 0.5 mM palladium sulphate-0.5mM silver sulphate aqueous solution (pl2).

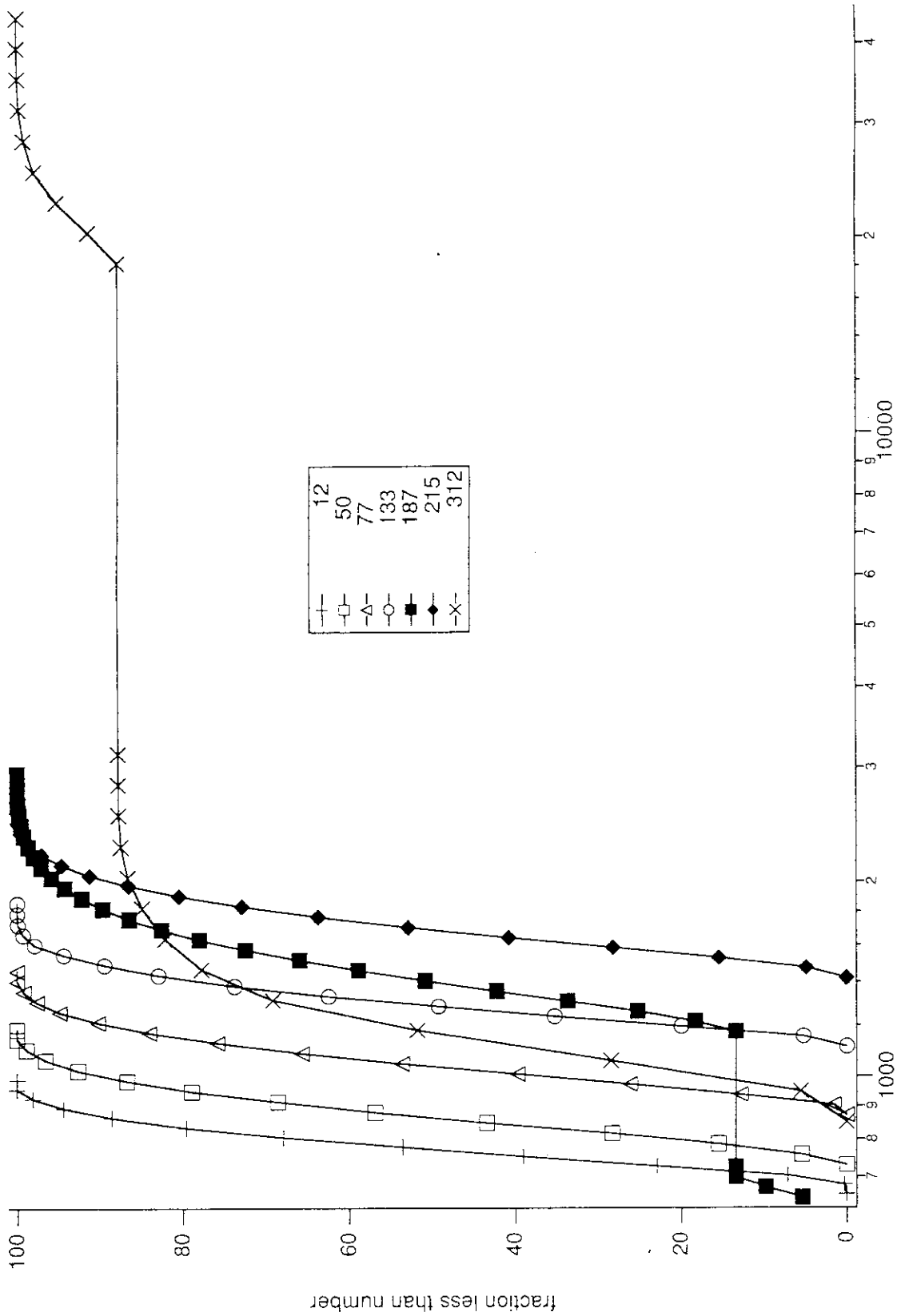


Fig. 11b. Fraction less than number as a function of particle size; cumulative index obtained by integration of the data shown in Fig. 11a.

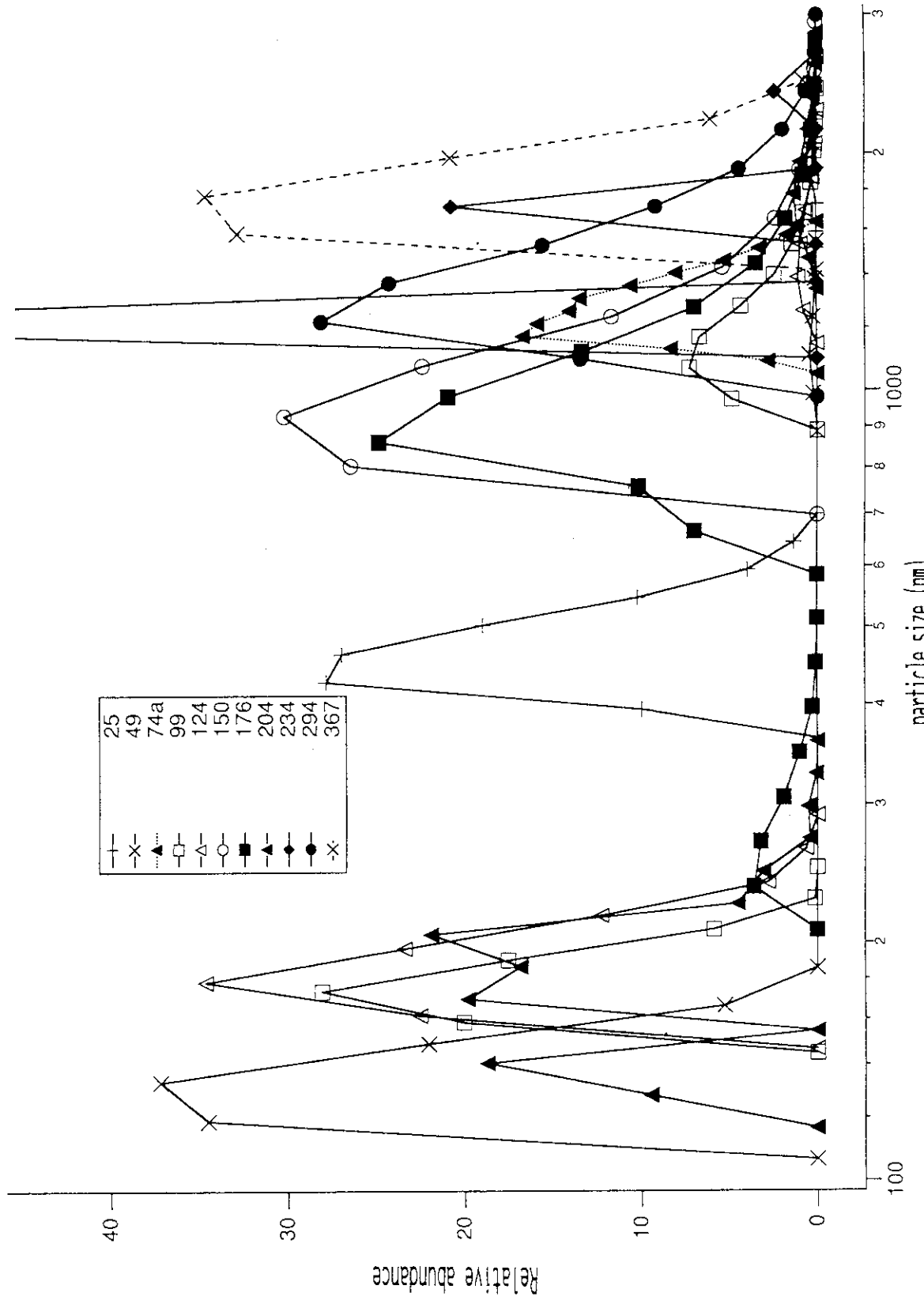


Fig. 12. Distribution of particle size obtained by DLS method measured at different waiting times after irradiation; numerals after symbols in the figure denote waiting time in minute after irradiation. Solution: 0.5 mM palladium sulphate-0.5mM silver sulphate aqueous solution (p13). (The same as in Fig. 11a to show reproducibility of the experiment)

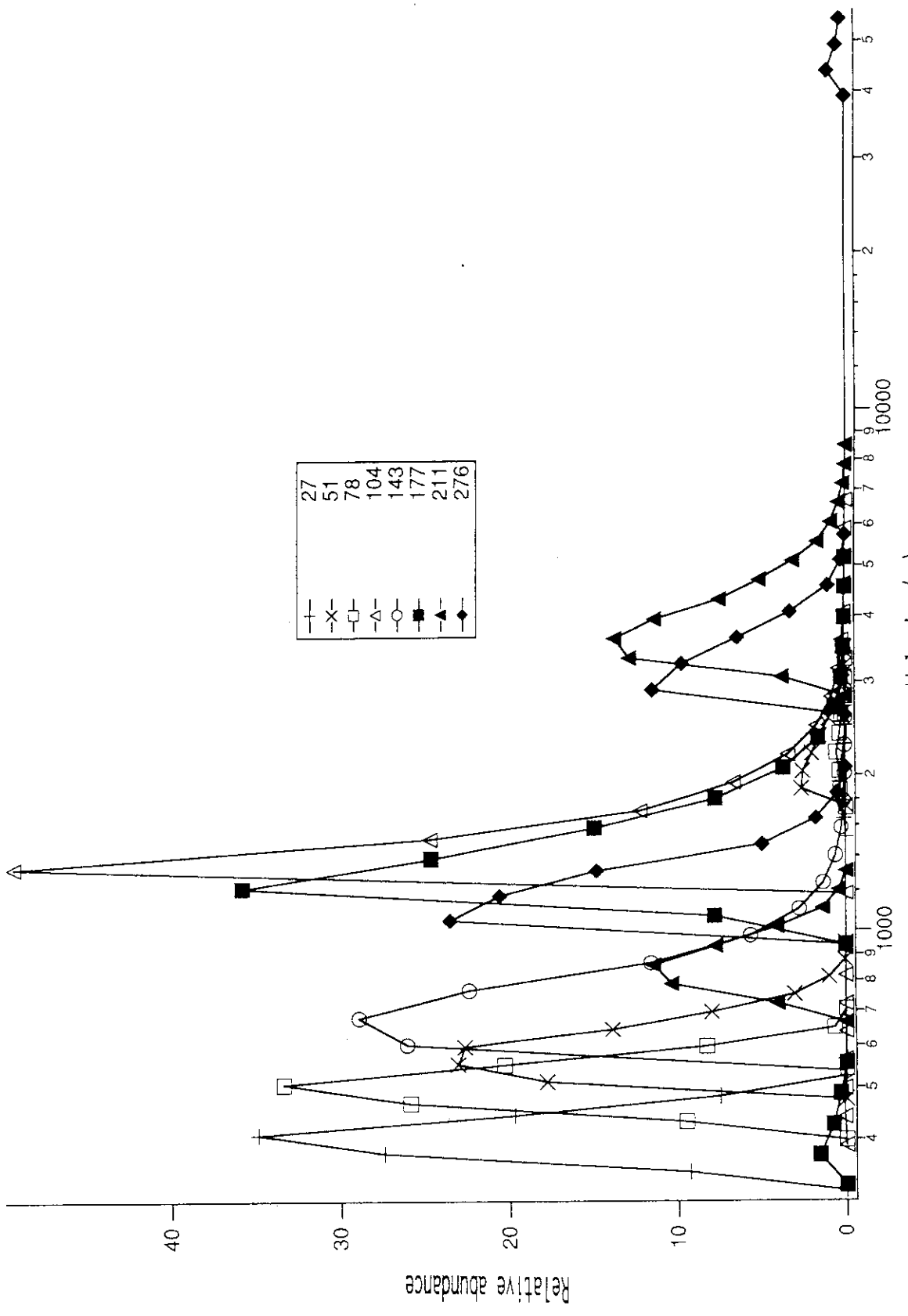
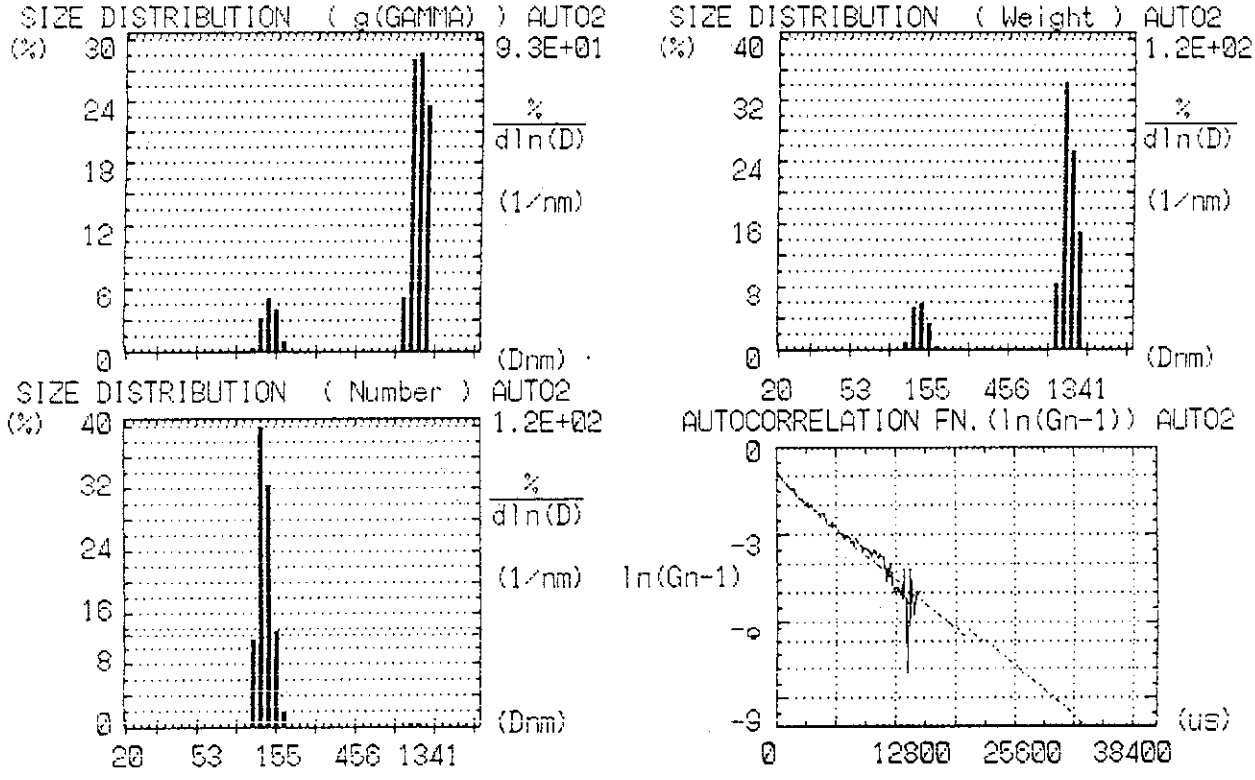


Fig. 13. Distribution of particle size obtained by DLS method measured at different waiting times after irradiation; numerals after symbols in the figure denote waiting time in minutes after irradiation. Solution: 0.5 mM palladium sulphate-0.5mM silver sulphate aqueous solution (p14). (The same as in Fig. 11a and Fig. 12 to show the reproducibility of the experiment)



P A R A M E T E R L I S T

DATE	93/03/30	G =	155.8 /sec
TIME	15:58:42	D =	4.4588D-09 cm2/sec
DATA NAME	P27	d =	909.6 nm
SAMPLING TIME(usec)	40	u/G^2=	2.0654E-01
ACUUM.TIME(times)	50	CUT (N)	5.00%, (S) 0 (L) 0
CORRE.CH(channel)	1024	D.min	20.0, D.max 2300
ANGLE (deg.)	90	Step	50
TEMPERATURE (°C)	18.1	Lambda	11.4
REFR.INDEX	1.3313	X-mode (log)	
VISCOSITY (cP)	1.051	Residual	0.0094
DATA TYPE	< T.D. >	DATA SET	odd
PHOTON COUNT	5577	RUN TIME	443 INTERVAL 0

	g(G) Aver+- S.D.	Weight Aver+- S.D.	Number Aver+- S.D.	dw/dn
1	142.2+- 15	137.5+- 14	133.2+- 14	
2	1066.5+- 103	1036.4+- 102	1007.9+- 96	
Tot	935.7+- 336	887.8+- 347	143.4+- 95	6.19

Fig. 14. An example of out put sheets from DLS analysis results; conditions of data acquisition are shown in the sheet; p27, 45 min after irradiation.

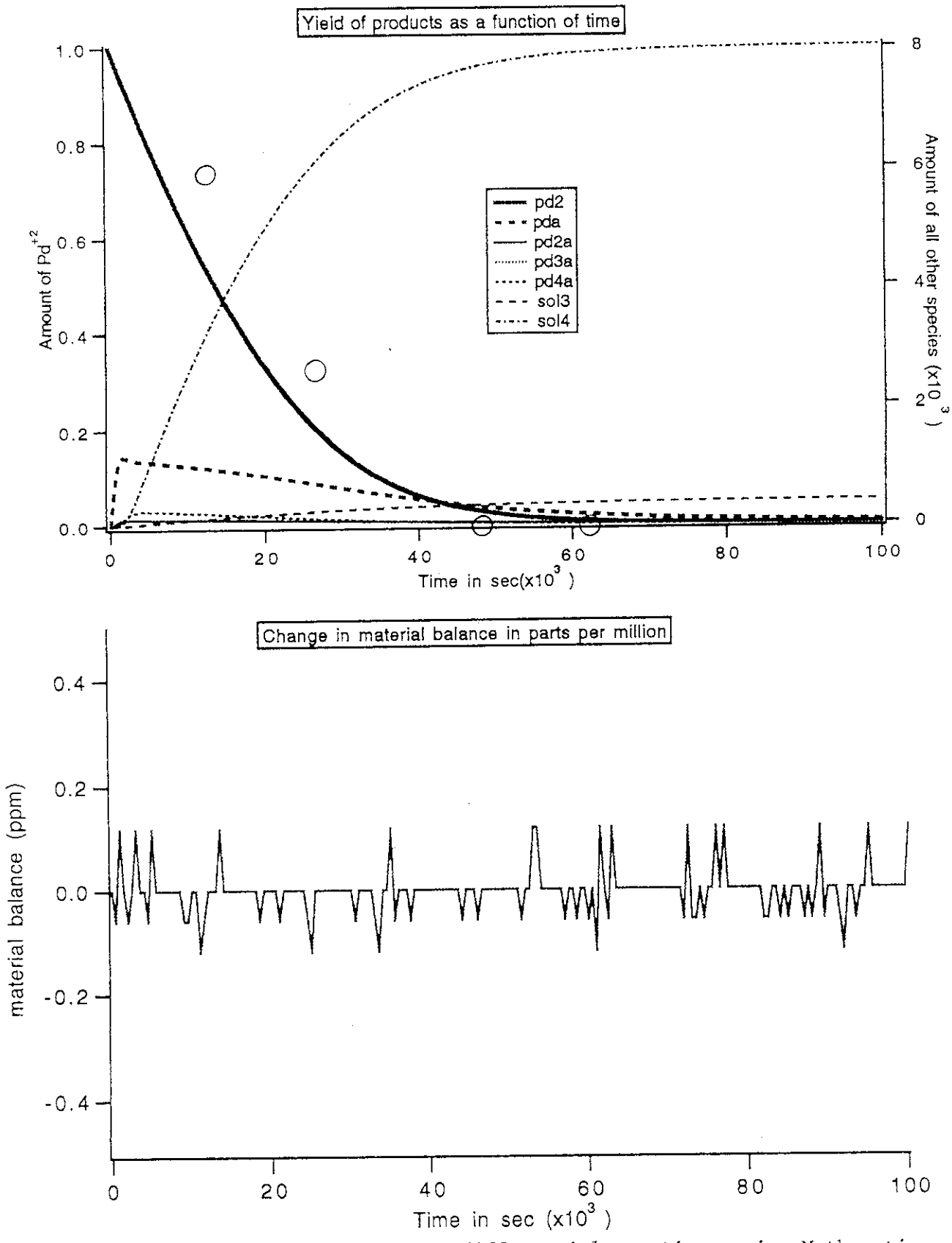


Fig. 15. Upper panel: solution to differential equations using Mathematica (see text and appendix 2 for the conditions of the solution); pd2 means Pd^{2+}; pda: cluster of average 30 palladium atoms; pdia: aggregate of i pda's, where i is 2, 3, 4; sol3 and sol4 mean precipitates of pda3 and pda4, respectively. Lower panel: Materi Material balance as a function of time.

APPENDIX 1 LITERATURE SURVEY

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APPENDIX 2 SETUP AND COMMANDS FOR THE SOLUTION OF DIFFERENTIAL EQUATIONS FOR THE FORMATION OF SOLID PARTICLES USING MATHEMATICA AND THE BASIC PROGRAM TO CONVERT SPECTRAL DATA TO O.D.-TIME DATA

Equations

```
pd2=pd2c'[t]==-k1 pd2c[t]/(pd2c[t]+const);
pda=pdac'[t]==k1 pd2c[t]/(pd2c[t]+const)/30-2 kaa pdac[t] ^2
                -k2aa pdac[t] pd2ac[t]-k3aa pdac[t] pd3ac[t];
pd2a=pd2ac'[t]== kaa pdac[t]^2 -k2aa pdac[t] pd2ac[t];
pd3a=pd3ac'[t]==k2aa pdac[t] pd2ac[t]-k3aa pdac[t] pd3ac[t]-s3 pd3ac[t];
pd4a=pd4ac'[t]==k3aa pdac[t] pd3ac[t]-s4 pd4ac[t];
sol3=sol3'c[t]==s3 pd3ac[t];
sol4=sol4'c[t]==s4 pd4ac[t]
```

Initial Conditions

```
pd2=1.00;pda0=pd2a0=pd3a0=pd4a0=sol30=sol40=0;const=1
```

Rate Constants

```
kaa=.2;k2aa=k3aa=2;s3=.0001;s4=.00128
dst=.235;gval=1.5;drt=dsr 1000000 .00001/(1.6 10^19)/3600;
k1=dsr gval 10000/(6.023 10 ^23)
```

```
NDSolve[ {pd2,pda,pd2a,pd3a,pd4a,sol3,sol4,
pd2c[0]==pd20,pd2ac[0]==pda0,pd2ac[0]==pd2a0
pd3ac[0]==pd3a0,pd4ac[0]==pd4a0,sol3c[0]==sol30,sol4c[0]==sol40 } ,
 {pd2,pdac,pd2ac,pd3ac,pd4ac,sol3c,sol4c} ,  {t,0,20000 } ]
tv=20000; (pd2[tv] + pdac[tv] 30 + pd2ac[tv] 60 + pd3ac[tv] 90 + pd4ac[tv] 120
+sol3c[tv] 90 + sol4c[tv] 120)/.%13
```

Glossary of symbols

kaa, k2aa, k3aa: rate constants, values are temporally assumed.

s3, s4: sedimentation rate, or removal time of a particle (travelling down with a velocity according to Stokes' law) from optical measurement zone (2 cm): s4=0.00128 se^{-1} for a particle of a diameter of 1 μm, denisty=12.8 g/cm^3. The s3 is a temporally assumed value.

dsr: dose rate, 0.235 Mrad/h

gval: G value of initial disappearance of Pd^{2+} (pd2)= 1/30 of G value of pda formation, $G_i(-Pd^{2+})$, assumed to be 1.5 so that observed concentrations at

time t during irradiation (shown in Fig. 15 with ○ , P#0HB1, P#0IB1, P#I0B2, and P#0GB1 in Table A-3 of [1]) are reasonably close to the calculated pd2 line. const: The $G_i(-Pd^{2+})$ becomes small when the concentration of Pd^{2+} becomes small because reduction of Pd^{2+} competes solvated electrons with other species. Therefore, this constant is necessary in order to asymptote $G_i(-Pd^{2+})$ to zero when concentration of Pd^{2+} reaches zero.

```
10 REM PROGRAM TO TRANSFER DATA FROM ASCII FILES CREATED ON SPEC
20 REM SPECTROMETER AND AVERAGE 700 NM POINTS
30 REM WRITTEN CDJ 31/3/1993
40 INPUT "Please enter 1 for Macintosh, 2 for OASYS";DEST
50 IF DEST <1 OR DEST > 2 THEN GOTO 40
60 AS$=".ASC"
70 REM INITIAL TIME POINT AND TIME BETWEEN POINTS ARE READ IN
80 REM USING TZERO AND STEPTIME
90 INPUT "Output file name (please remember DRIVE LABEL)";OUTNAME$
100 OPEN OUTNAME$ FOR OUTPUT AS #2
110 IF DEST =2 THEN   FOR II=1 TO 10:PRINT #2,"":NEXT II
120 REM FILES WILL BE ASSUMED TO BE OF THE FORM
130 REM FILENAME##.ASC WHERE ## ARE DIGITS 0-9
140 INPUT "File name to be read (Please remember DRIVE)";GEORGE$
150 INPUT "Time zero ";TZERO
160 INPUT "Time step ";STEPTIME
170 FOR I= 0 TO 99
180 TAG$=STR$(I)
190 NC=LEN(TAG$)
200 REM IT IS NECESSARY TO STRIP OFF BLANK FROM STR$
210 TAG$=RIGHT$(TAG$,NC-1)
220 IF I<10 THEN TAG$="0" +TAG$
230 REM PUT IN 0 FOR 00 TO 09
240 TEMP$=GEORGE$+TAG$+AS$
250 ON ERROR GOTO 400
260 OPEN TEMP$ FOR INPUT AS #1
270 PRINT "FILE FOUND FOR ";I
280 SUM = 0
290 FOR J= 1 TO 10
300 INPUT #1,WL,VALUE
310 SUM = SUM + VALUE
320 NEXT J
330 SUM = SUM/10
340 TIME=TZERO + I*STEPTIME:PRINT TIME,SUM
350 IF DEST = 2 THEN PRINT #2,"           ";
360 PRINT #2,TIME,SUM
370 IF DEST = 2 THEN PRINT #2,""
380 CLOSE #1
390 GOTO 420
400 REM DUMMY STATEMENT
410 RESUME 420
420 NEXT I
430 INPUT "IF YOU WISH TO ADD ANOTHER SEQUENCE TO FILE ENTER 1";YN
440 IF YN=1 THEN GOTO 140
450 CLOSE #2
460 PRINT:PRINT "Data are saved in file ";OUTNAME$
470 PRINT "Good luck in your data analysis"
480 END
```