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ENTITLED GOLD SOL FORMATION MECHANISMS: COMPETITIVE BINDING OF

CITRATE AND AURIC ACID ANIONS

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Gold Sol Formation Mechanisms:
Competitive Binding of Citrate and Auric Acid Anions

by

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Section One:
INTRODUCTION

Colloidal gold sols have been repeatedly used to investigate the behavior of colloid systems. In the mid nineteenth century, Faraday investigated gold sol stability and, fifty years later, Mie applied his light scattering theory to account for particle size related color changes in gold suspensions.[1, 2] In recent years, colloidal gold systems have been employed in biotechnology to tag cellular components.[3] Still, gold sols are most frequently used as a medium to study the basic flocculation kinetics and stability of colloidal systems can be understood.[4, 5]

The familiar precipitation of gold crystals by the reduction of $AuCl_4^-$ with trisodium citrate is a classic example of gold sol growth. J. Turkevich has accumulated the most thorough data on this reaction and the ensuing colloidal gold formation and behavior.[6-10] Others, such as Takiyama and Frens, have attempted to complete the model of gold sol growth.[11,12] However, there is a glaring peculiarity of gold sol formation which previous studies have failed to explain. Several researchers have documented that gold colloid growth is characterized by the initial presence of large aggregates which eventually fall apart, resulting in a stable solution of uniform small particles.[13-19] This size change is characterized a color change from black to purple to red. This behavior certainly does not coincide with the classical LaMer growth model, in which colloidal growth begins with a short burst forming many small nuclei which then flocculate into larger and larger aggregates.[20]

Recently, however, Grieser and Zukoski have postulated that the unexpected growth pattern can be explained by a competitive binding mechanism in which the $AuCl_4^-$ and citrate anions compete for sites on the colloidal gold crystals.[21] The Zukoski-Grieser model begins where Turkevich left off, more specifically providing an alternative to the LaMer model. The theory predicts that the size and stability of the gold particles is the direct result of which and how much citrate or auric acid anion binds to the gold surface. The model further explains that the surface potential at the gold - water interface changes as the reaction proceeds and these changes are caused by the adsorption and desorption of citrate and $AuCl_4^-$ anions on the gold particles. Grieser and Zukoski have developed this theory after measuring gold surface potentials directly with an atomic force microscope. They have found that the gold surface potential does indeed change upon the presence of $AuCl_4^-$ and trivalent citrate.[22] However, until now, this theory has not been tested on a gold sol system.

The Grieser-Zukoski model envisions a chain of events which neatly account for observed particle color and size changes. After the initial nucleation, $AuCl_4^-$ anions preferentially bind to the gold surfaces and, now catalyzed, are reduced. At this point the particles are unstable and flocculate into 100-200 nm aggregates.[23] However, the model postulates that as the

$AuCl_4^-$ is consumed, citrate anions move to occupy the vacant sites, forming a steric-electrostatic barrier to attraction, which causes the aggregates to fall apart into small, 25 nm particles. Addition of $HAuCl_4$ to a stable gold sol should have the $AuCl_4^-$ anions to displace the citrate, inducing aggregation. New particles should form on existing gold surfaces, and as the $AuCl_4^-$ is reduced, the citrate will re-bind, once again resulting in a solution of stable, small particles. The difference between the original sol and the final sol should be in number density of particles only. Some time after adding back the $AuCl_4^-$, the size and color (absorbance) of the sol should become the same as before the reaction.

Thus, to provide further support to the competitive binding hypothesis, a series of experiments involving actual gold sols was commissioned. The following report details and analyzes further experiments which intend to support the Zukoski-Grieser competitive binding mechanism. Briefly, the experiments involved adding back amounts of $AuCl_4^-$ and monitoring changes in particle absorbance and size. After a description of the experimental procedure, Section Three presents the results. Section Four offers an analysis of the tests and is followed by several conclusions.

Section Two:
EXPERIMENTAL PROCEDURE

2.1 Gold Sol Formation

Following the procedure described by Turkevich, the gold sols were formed by a reducing $AuCl_4^-$ with trisodium citrate.[24] Specifically, aqueous solutions of hydrotetrachloric auric acid hydrate ($HAuCl_4 \bullet 3H_20$) and trisodium citrate ($Na_3C_5H_6O_7$) were mixed at 70 °C. Upon reaction, metallic gold precipitates in colloidal dimensions. All gold sols used in experiments were made in 250 - 500 ml amounts using 2.4×10^{-4} M $HAuCl_4$ and 1.6×10^{-3} M $Na_3C_5H_6O_7$. Typically, 250 ml of 2.4×10^{-4} M $HAuCl_4$ solution in a round-bottom flask was brought to thermal equilibrium in a 70 °C water bath. Next, 1 ml of 0.4016 M $Na_3C_5H_6O_7$ was added. For Reaction Series Three, the base sol concentration was lowered with $HAuCl_4$ concentrations of 1.2×10^{-5}, 2.4×10^{-5} and 6.0×10^{-5} M. Even in the lower concentration sols, the citrate concentration remained constant at 1.6×10^{-3} M.

The reaction is highly temperature dependent and is complete in about 50 minutes at 70 °C or about 6 hours at room temperature.[25] The solution, initially clear, slowly turns gray, blue, violet, purple, and then suddenly red as the gold particles form, flocculate and fall apart. The final sol color is a deep ruby red, corresponding to a particle size of about 20 nm. The more weakly concentrated sols had a pink to rose hue after a complete reaction, although particle sizes remained in the 20 - 30 nm range.

To achieve absolute cleanliness, all glassware was soaked in aqua regia for one hour and then rinsed with deionized water prior to use. All water used in solutions and used in cleaning was 0.2 μm filtered deionized water provided by a Barnstead Nanopure II filtering system. The hydrotetrachloric auric acid hydrate was obtained from Aldrich Chemical Co., while the citrate was purchased from Fisher Scientific.

2.2 Absorbance Spectroscopy

Gold sol absorbance was measured using a Spectronic 1001 spectrophotometer. The cuvettes were quartz with a 1 cm path length and contained about 2 ml of solution. Absorbance curves were generated by measuring absorbance at 10 nm intervals over a 490 to 630 nm range. Peak Absorbance was established by running the machine over the said range at 0.1 nm intervals. A "peak find" function on the machine performed this task.

2.3 Dynamic Light Scattering

Dynamic light scattering was performed was used to size the gold particles in solution. The system was a Brookhaven Instruments BI-2030 AT correlator with a 35 mW He-Ne Laser at a wavelength of 632.8 nm. In addition to the correlator, the apparatus consisted of a gonimeter, a photomultiplier tube, optical lenses and filters. All were interfaced with a personal computer for data acquisition and analysis. The software, supplied by Brookhaven, transformed the photon signals into an autocorrelation function for scattered light, from which the diffusivity of the particles was obtained. The average particle size was calculated using the Stokes-Einstein equation:

$$D_p = k_B T / 6\pi\eta a \qquad (1)$$

where k_B is the Boltzmann constant, T is temperature, η is the medium viscosity, and a is the particle radius.[26] Each sample was measured at three different scattering angles (60°, 90°, 120°) and the values reported are an average of these three measurements. It should be noted that, early in the reaction, the polydispersity was larger and thus the particle size did vary with the angle of measurement. However, the average value from three angles was still used.

2.4 Adding Back $HAuCl_4^-$

The actual experiments were performed in much the same way as the making of the gold sols. As was described in the introduction, the idea was to add back various amounts of $AuCl_4$- to existing gold sols and follow particle size and absorbance. All reactions were run with a 100 ml volume of gold sol. Reaction Series One and Three were run at 70 °C (the temperature at which the sols were formed), while reaction Series Two was performed at 25 °C. The reaction vessel was a 250 ml volumetric flask with a magnetic stir bar added. Over the course of this investigation, many different amounts of $AuCl_4^-$ were added back, ranging from 5 to 2000% of the original amount of $AuCl_4^-$. The citrate concentration was held constant in these experiments, at 1.6×10^{-3} M.

2.4.1 Reaction Series One

In these reactions, eleven separate flasks containing 100 ml amounts of gold sol at a concentration of 2.4×10^{-4} M in $HAuCl_4$ and 1.6×10^{-3} M $Na_3C_5H_6O_7$ were heated to 70 °C. First, the absorbance of the base sols was measured so a t(0) absorbance could be established. After the sol came to thermal equilibrium, different amounts of $HAuCl_4$ were added back to the sols. Table One summarizes the additions. In general, the amount added back reflects a specific percentage of $AuCl_4^-$ added to the original sol. The $HAuCl_4$ stock solution was 2.4×10^{-4} M.

Table One:

Reaction Series One Addition Scheme

Reaction	$[HAuCl_4]_0$ (mol/L)	[Citrate] (mol/L)	$HAuCl_4$ added (ml)	% of original $HAuCl_4$
1	2.4×10^{-4}	1.6×10^{-3}	5	5
2	2.4×10^{-4}	1.6×10^{-3}	10	10
3	2.4×10^{-4}	1.6×10^{-3}	15	15
4	2.4×10^{-4}	1.6×10^{-3}	20	20
5	2.4×10^{-4}	1.6×10^{-3}	25*	75
6	2.4×10^{-4}	1.6×10^{-3}	50	50
7	2.4×10^{-4}	1.6×10^{-3}	40	40
8	2.4×10^{-4}	1.6×10^{-3}	50	50
9	2.4×10^{-4}	1.6×10^{-3}	60	60
10	2.4×10^{-4}	1.6×10^{-3}	70	70
11	2.4×10^{-4}	1.6×10^{-3}	80	80

* Another 50 ml was added after 2.75 hours.

Following addition, the absorbance and size of the particles was followed over time. Time between samples was 10 minutes early in the reaction, 15 minutes midway through, and then every hour for five hours. All raw data is tabulated in Appendix A. Samples were quenched in ice to halt the reaction long enough for measurement. Due to the high temperature dependence of the reaction, "quenching" in ice allows for accurate results, as the sample is temporarily "frozen" for about 3 hours.[27]

2.4.2 Reaction Series Two

These reactions were very similar to those in reaction Series One. However, instead of just adding $HAuCl_4$ back, water was added also to adjust the concentration while keeping volume constant. Also, these reaction were run at a constant temperature of 25 °C, as opposed to 70 °C. Initial sol volume was 100 ml to which 100 ml of $HAuCl_4/H_20$ mixture was added, bringing the total volume to 200.8 ml, including the citrate, which was added to preserve the 1.6 x 10-3 M concentration. Table Two summarizes these reactions.

Table Two:

Reaction Series Two Addition Scheme

Reaction	$[HAuCl_4]_f$ (mol/L)	[Citrate] (mol/L)	$HAuCl_4$ Added (ml)	Citrate Added (ml)	H_2O Added (ml)
1	1.2×10^{-6}	1.6×10^{-3}	1	0.8	99
2	2.39×10^{-5}	1.6×10^{-3}	20	0.8	80
3	4.78×10^{-5}	1.6×10^{-3}	40	0.8	60
4	8.37×10^{-5}	1.6×10^{-3}	70	0.8	30
5	1.20×10^{-4}	1.6×10^{-3}	98	0.8	2
6	9.31×10^{-4}	1.6×10^{-3}	40*	0.8	60
7	2.33×10^{-4}	1.6×10^{-3}	100*	0.8	0

* $HAuCl_4$ stock solution was 4.871×10^{-3} M. For all others it was 2.4×10^{-4} M.

Following the addition of the $HAuCl_4$, samples were taken at various time intervals (approximately every 15 to 30 minutes) and after quenching, their absorbance and size were analyzed. Note that, prior to the reaction, the absorbance and size of the base sols was measured so a t(0) curve could be established. All absorbance and size data is attached in Appendix B.

2.4.3 Reaction Series Three

In these reactions, the base sols were lower in $HAuCl_4$ concentration. Three separate concentrations were investigated: 1.2×10^{-5}, 2.4×10^{-5} and 6.0×10^{-5} M $HAuCl_4$. Each had a citrate concentration of 1.6×10^{-3} M. Again, the absorbance and size of the base sols was measured to establish a t(0) reference. For each concentration, a 100 ml volume was warmed to 70 °C and allowed to come to thermal equilibrium. Next, each solution was brought to the standard $AuCl_4^-$ concentration of 2.4×10^{-4} M with the addition of $HAuCl_4$. By adding a minuscule amount (µL) of 0.4016 M citrate solution, citrate concentration remained constant though volume was slightly increased. Table Three details the additions.

Table Three:

Reaction Series Three Addition Scheme

$[HAuCl_4]_0$ (mol/L)	$[Citrate]_0$ (mol/L)	$[HAuCl_4]_f$ (mol/L)	$HAuCl_4$ Added (ml)	Citrate Added (µL)
1.2×10^{-5}	1.6×10^{-3}	2.4×10^{-4}	4.92	19.7
2.4×10^{-5}	1.6×10^{-3}	2.4×10^{-4}	4.67	18.7
6.0×10^{-5}	1.6×10^{-3}	2.4×10^{-4}	3.89	15.6

Samples were extracted during the reaction at 5, 10, 15, 30, 45, 60, 90 and 120 minutes. Next, they were quenched in ice before the particle size and absorbance was measured. All raw reaction Series Three data is attached in Appendix C.

Section Three:

RESULTS

3.1 Reaction Series One

Only absorbance data was taken during the Series One runs. For reactions 7 - 11, the absorbance spectrum and the peak absorbance was tracked as the reaction proceeded. The absorbance spectra offers a clear picture of the reaction kinetics, especially for reactions 7 - 11, where a larger amount (between 40 - 100% of the original) of $HAuCl_4$ was added back. A typical absorbance curve is shown in Figure 2, where the absorbance spectrum of Series One, Reaction 11 is shown over time. Figure 3 is a plot of the peak absorbance for the same reaction. All other reaction data and plots are available in Appendix A.

Figure 1

Reaction 11 Absorbance vs. Time

80 ml of 2.4×10^{-4} M $AuCl_4^-$ added back

to 100 ml base sol (2.4×10^{-4} M $AuCl_4^-$ + 1.6×10^{-3} M Citrate) at 65 °C

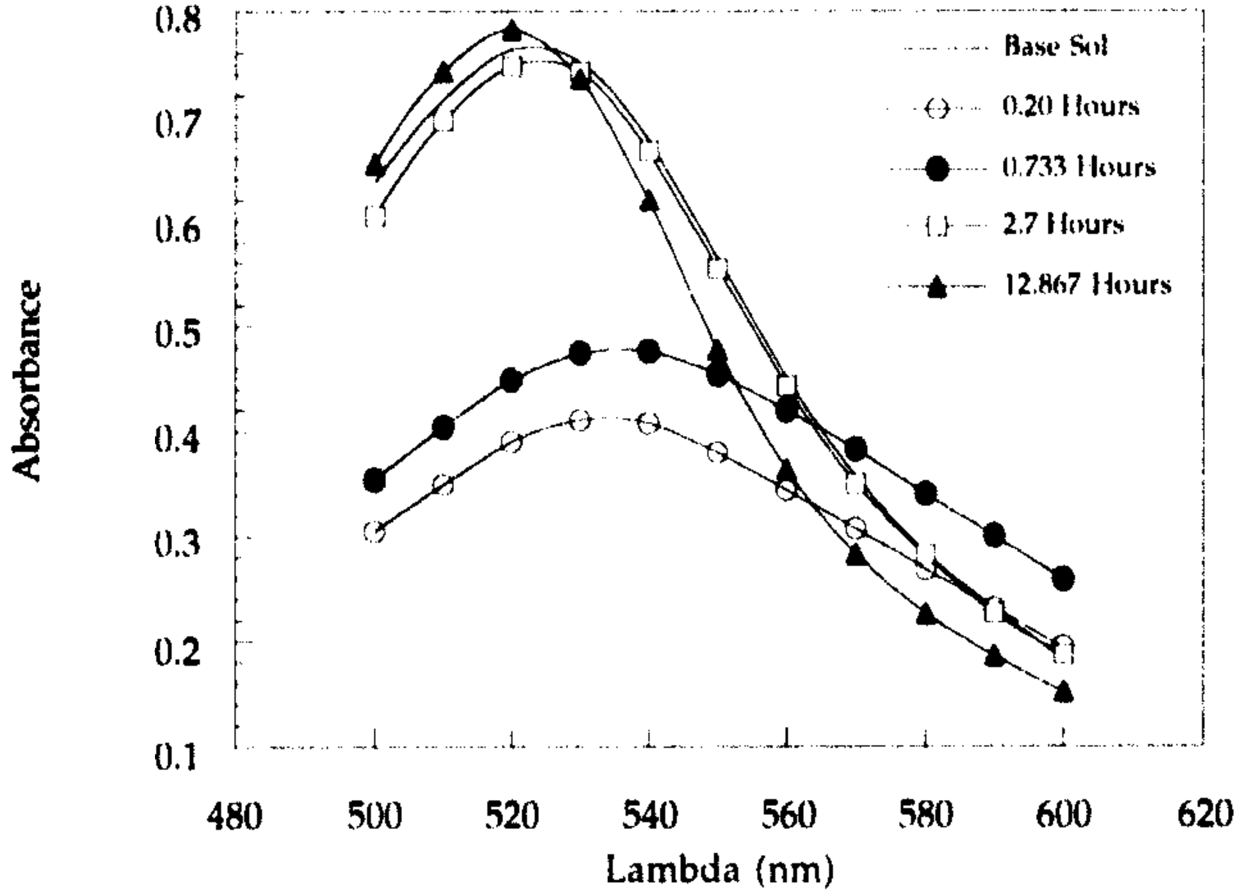


Figure 2
Reaction 11 Peak Absorbance vs. Time

80 ml of 2.4 x 10^{-4} M $AuCl_4^-$ added back to 100 ml base sol (2.4 x 10^{-4} M $AuCl_4^-$ + 1.6 x 10^{-3} M Citrate) at 65 °C

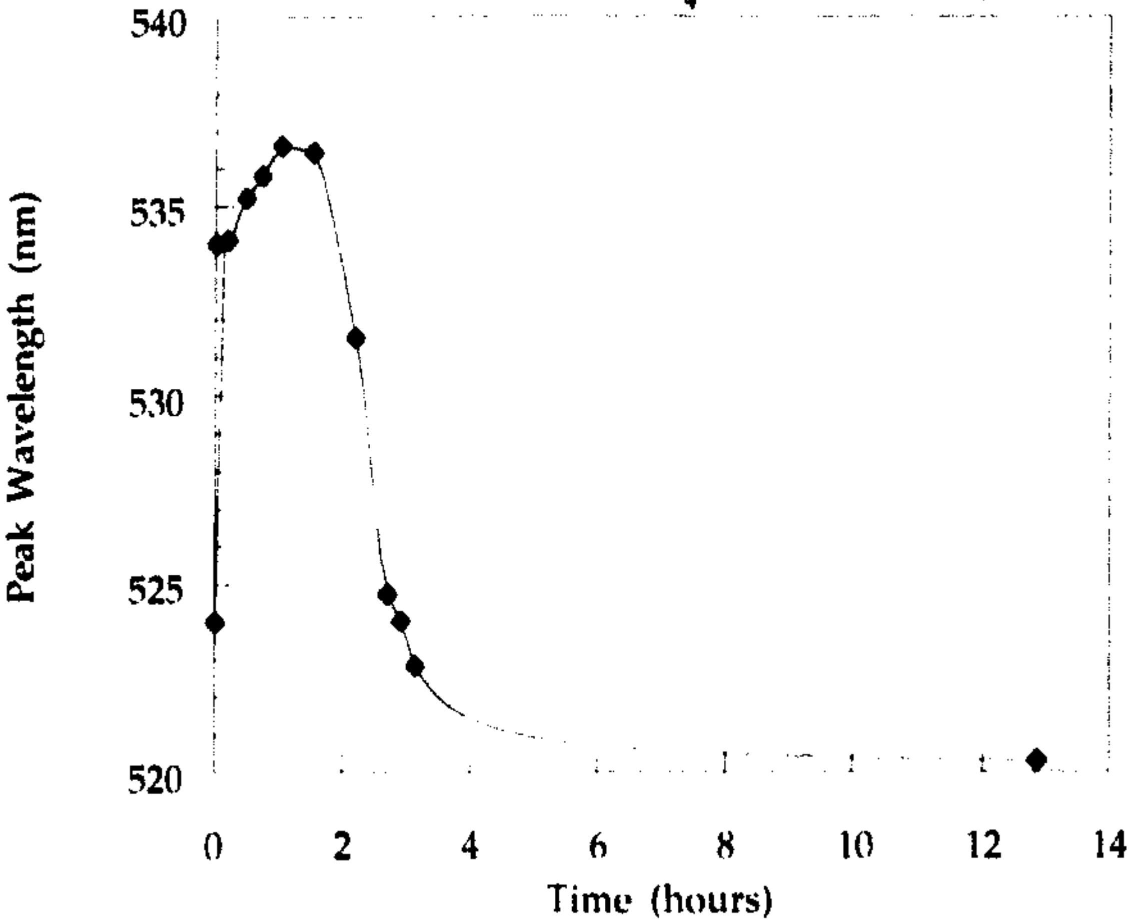


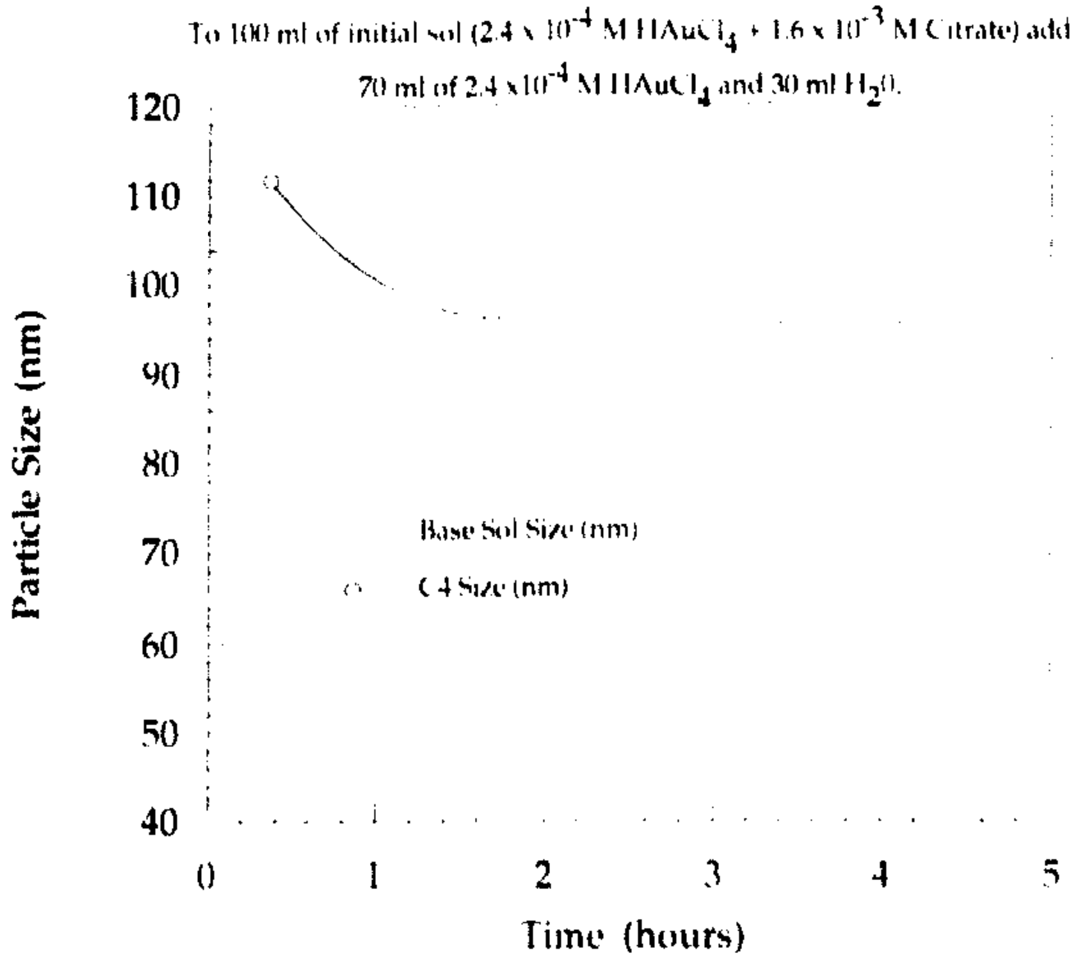
Figure 1 reveals the expected upward shift in the absorbance spectrum and also shows a broadened curve, which reflects greater sol polydispersity. Also, the absorbance intensity decreases by 50 % in the first 12 - 15 minutes. The absorbance intensity, which falls due to the initial sol dilution upon addition of 80 ml $HAuCl_4$, recovers as additional gold is reduced and the number of particles increases. Figure 2 isolates the upshift in $\lambda_{max.}$ over time, and shows a change from 524.0 nm to a maximum of 536.6 nm shortly after one hour.

The remaining reactions in this series exhibited similar behavior, except for reactions 1 -4, which saw only a slight absorbance peak upshift. In reactions 1 -4, less than 30% of the original amount of 2.4×10^{-4} M $HAuCl_4$ was added back, seemingly not enough to displace the citrate on existing gold particles.

3.2 Reaction Series Two

This group of reactions, very similar to the first series, exhibited the same absorbance peak shift and spectrum widening as previously. Again, each absorbance plot shows a dramatic intensity decrease due to dilution, a change which recovers with time. However, all changes occur over a much longer time frame , as the reaction was run at 25 ^{0}C. As the plots in Appendix B reveal, many inconsistencies were produced during these runs. However, the size versus time data for Reactions 1 - 4 demonstrate similar trends. Figure 3 below is an example.

Figure 3
Reaction 4 Size vs. Time

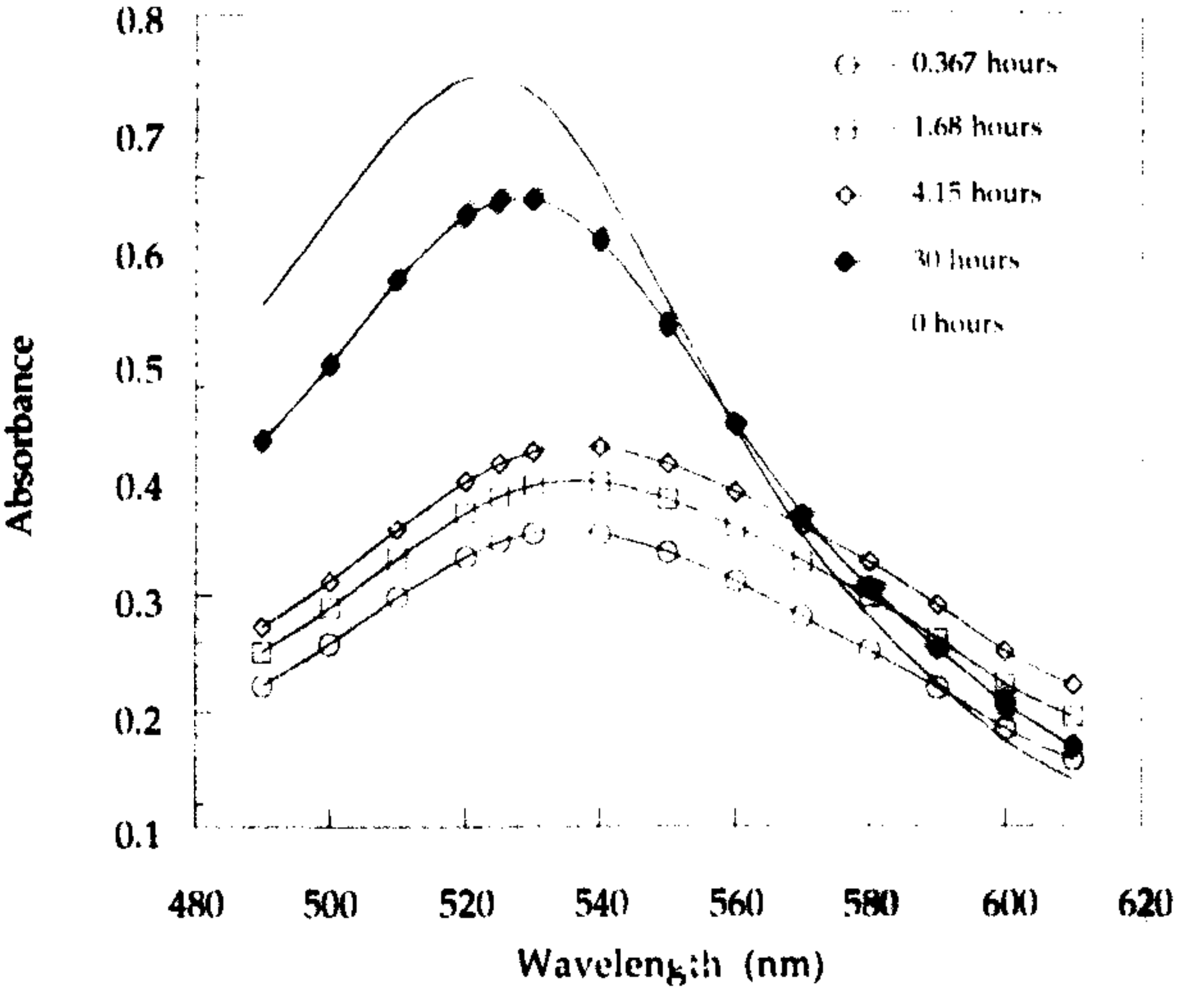


To 100 ml of initial sol (2.4×10^{-4} M $HAuCl_4$ + 1.6×10^{-3} M Citrate) add 70 ml of 2.4×10^{-4} M $HAuCl_4$ and 30 ml H_2O.

Note the initial jump in particle size from about 43 nm to approximately 112 nm. As time progresses, the particles slowly begin to shrink. Recall that the reaction was run at a cool 25 °C , so the shrinking process is slow. After five hours, the average particle size is about 95 nm. However, after roughly 30 hours, the absorbance peak, and thus the particle size, is approaching its original value. This change is seen in Figure 4.

Figure 4
Reaction 4 Absorbance over Time

To 100 ml of initial sol (2.4×10^{-4} M $HAuCl_4$ + 1.6×10^{-3} M Citrate) add 70 ml of 2.4×10^{-4} M $HAuCl_4$ and 30 ml H_2O.



Reactions 1 through 5 yielded about the same results. However, reactions 6 and 7 gave strange unexpected size values and changes. The absorbance curve changes were peculiar also. This may be due to the fact that amounts of 4.871×10^{-3} M $HAuCl_4$ was added back rather than the weaker 2.4×10^{-4} M $HAuCl_4$ solution. Even so, reactions 6 and 7 themselves differ in size trends, and the values reported are not understood. It is very likely that a human accounting error or operating error is the source of this confusion.

3.3 Reaction Series Three

These reactions provide by far the most complete data. Absorbance spectra, peak absorbance and particle size were all monitored over the course of the reaction. One unusual feature of these reactions is that the starting gold sols were very low in concentration. Perhaps because of this, the absorbance data for reactions 1 and 2 reveals a starting sol absorbance peak near 595 nm. Thus, during the course of the reaction, the absorbance peak shifts down, not up. Furthermore, the dynamic light scattering results show that the base sols for reactions 1 and 2 have an average particle size of 45 nm, which is somewhat high. The size data does show an increase followed by a decrease in particle size over the course of the reaction. However, these trends are in keeping with the competitive binding hypothesis. Reaction 3 provided the expected behavior, with an upshift followed by a downshift in absorbance peak; a narrowing of the absorbance curve; and an increase then a decrease in gold particle size. While all the Series Three data is plotted and tabulated in Appendix C, the peak absorbance and size changes for reaction 3 can be viewed in Figures 5 and 6.

Figure 5
Reaction 3 Peak Absorbance vs. Time

Base Sol ($6.0e{-}5$ M $HAucl_4$ + $1.6e{-}3$ M $Na_3C_6H_5O_7$) brought
to $2.4e{-}4$ M $HAucl_4$ and $1.6e{-}3$ M $Na_3C_6H_5O_7$.

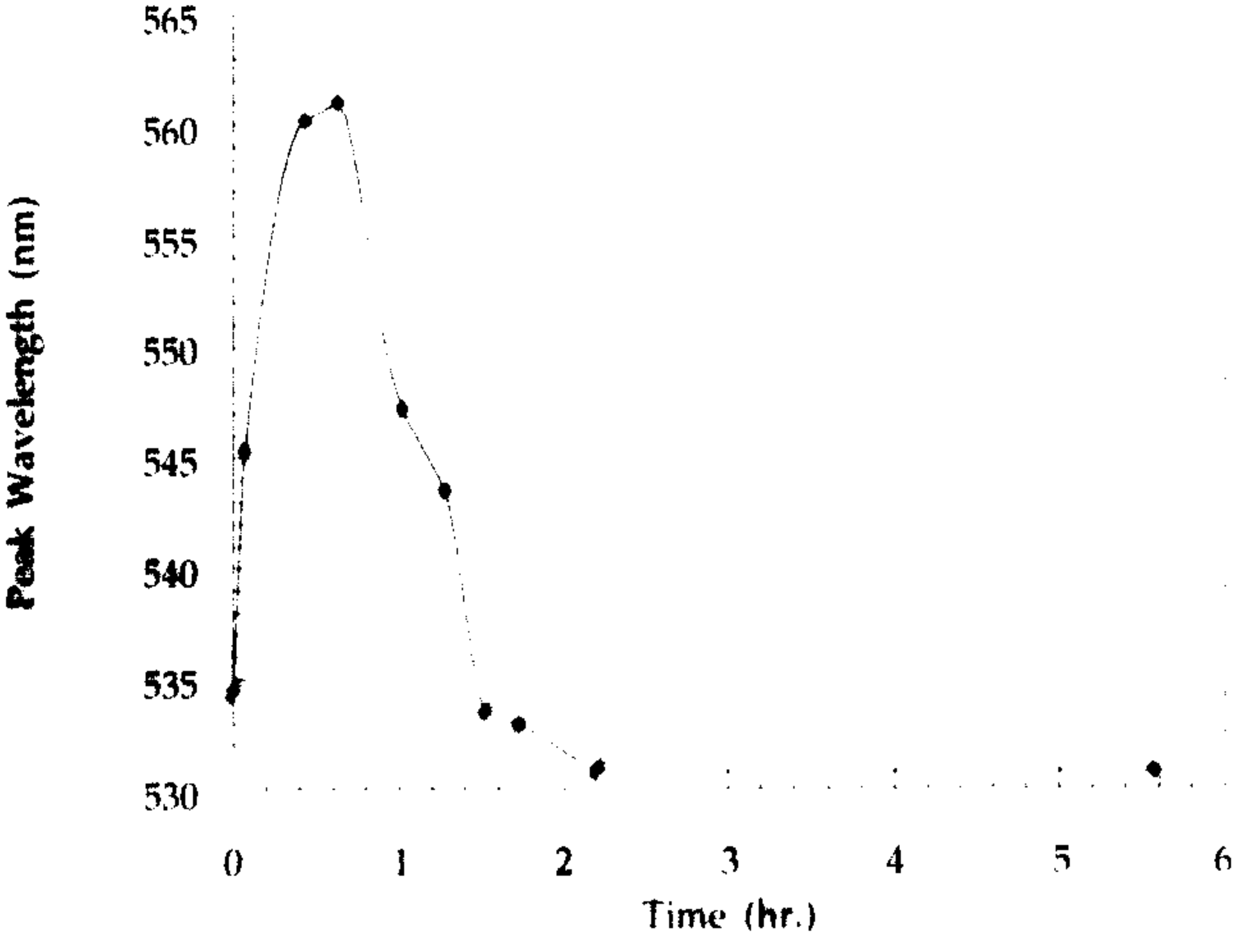
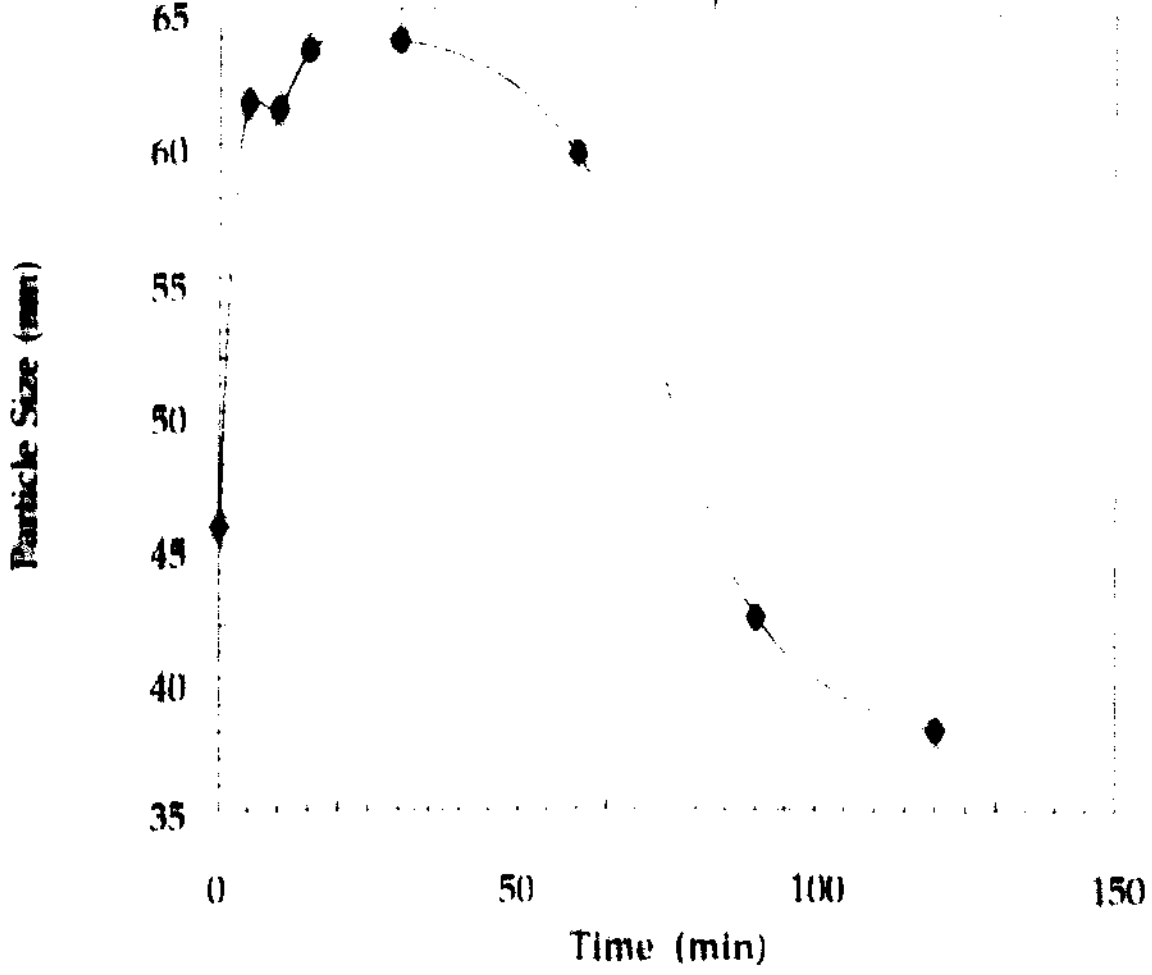


Figure 6
Reaction 3 Size vs. Time

Base sol (6.0×10^{-5} M $HAuCl_4$ + 1.6×10^{-3} M Citrate) brought to 2.4×10^{-4} M $HAuCl_4$ and 1.6×10^{-3} M Citrate



Section Four:
DISCUSSION

Recall that the $AuCl_4^-/C_5H_6O_7^{3-}$ competitive binding mechanism suggests that in the early stages of sol growth, the $AuCl_4^-$ preferentially adsorbs on the surface of the gold particles. During this time, the Van der Waal's and electrostatic forces are such that the particles flocculate into 100 to 200 nm clusters. However, as the $AuCl_4^-$ is reduced to Au^0, the citrate ions occupy the vacant surface sites until the gold units comprising the aggregates are surrounded by enough citrate to cause a steric-electrostatic short range repulsion. At this point, the flocculates fall apart into many uniform, small particles in the 25 nm size range. Upon addition of more $AuCl_4^-$, the stable, small particles should flocculate again as the $AuCl_4^-$ anions displace the citrate layer. Sol number density should initially decrease, then increase over that of the original sol, as the growth process is repeated.

It is clear, if just from inspecting Figures 1 - 6, that the Zukoski-Grieser competitive binding theory does account for nonclassical particle size and absorbance changes in the formation of colloidal gold sols. As the theory predicts, addition of more $HAuCl_4$ to a stable gold sol causes the particles to flocculate and then suddenly shrink back to near the original size. Such a change is evident in Figures 1 through 6 and in the majority of data contained in the Appendices. In Figure 1 and 2, the plots shows that when 80% more $AuCl_4^-$ is added to a sol that is 2.4×10^{-4} M in $HAuCl_4$ and 1.6×10^{-3} M in $Na_3C_5H_6O_7$, the absorbance peak shifts from 524 nm to a maximum at 536 nm and then ends up at 521 nm. In addition, the broadening and then the narrowing of the absorbance spectrum reflects the increase and then the decrease in the particle polydispersity (the increase and decrease in aggregate particles).

In addition, Figure 3 captures the large jump in particle size (from 542 to 112 nm) when 70% more $HAuCl_4$ is added to a gold sol at 2.4×10^{-4} M in $HAuCl_4$ and 1.6×10^{-3} M in $Na_3C_5H_6O_7$. This increase is followed by a slow decrease, which, as indicated by Figure 4, ends in a return to the original size. Again, the absorbance and size trends support the mechanism.

Figures 5 and 6 are similar plots which could perhaps be superimposed to reveal the same rate of change. This is in accordance with the Mie absorbance theory relating size to λ_{max}.[28] The size change resulting from the addition of 400% as much $AuCl_4$- is clear in Figure 6.

The above discussion generally treats an involved mechanism, but the test results offer solid qualitative proof of competitive adsorption between the auric acid and citrate anions.

Section Five:

CONCLUSIONS

Gold sol formation via the reduction of auric acid by trisodium citrate apparently occurs through a competitive binding mechanism in which the auric acid and citrate anions compete for sites on the gold crystals. The resulting colloidal stability fluctuations cause the particles to initially flocculate into large aggregates which shrink over the course of the reaction. The final sols are characterized by number of small, stable particles which remain separated by a short range steric-electrostatic force. The size and absorption results correlate this conclusion. This model at most replaces and at least supplements the classical model in which the gold particles are said to behave like hard spheres governed by the sum of Van der Waals and electrostatic forces.

Since this study is essentially a surface treatment of a complex phenomenon there is much room for future examination of this system. Surface potential measurements are a necessary starting point. Also, it is suspected that citrate is one of several reducing agents which may bind to the gold surface. Exploring alternative reagents would certainly assist in validating the Zukoski-Grieser competitive binding mechanism.

Acknowledgments

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APPENDICES

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Appendix A

Appendix B

Appendix C

Appendix D

APPENDIX A

Reaction Series One Data and Plots

Table 1

Reaction 1 Absorbance Data

5 ml of 2.4×10^{-4} M $AuCl_4^-$ added back to

100 ml base sol (2.4×10^{-4} M $AuCl_4^-$ + 1.6×10^{-3} M Citrate) at 65 °C

λ (nm)	0 hr	0.283 hr	0.767 hr	2.22 hr
490	0.548	0.549	0.549	0.522
500	0.629	0.633	0.632	0.599
510	0.707	0.715	0.714	0.676
520	0.748	0.759	0.760	0.720
525	0.744	0.757	0.758	0.720
530	0.723	0.737	0.738	0.703
540	0.637	0.649	0.650	0.628
550	0.519	0.527	0.528	0.520
560	0.407	0.413	0.412	0.418
570	0.320	0.324	0.323	0.339
580	0.256	0.260	0.259	0.281
590	0.203	0.208	0.206	0.234
600	0.166	0.171	0.171	0.200
610	0.131	0.138	0.136	0.168

Table 2

Reaction 2 Absorbance Data

10 ml of 2.4×10^{-4} M $AuCl_4^-$ added back to

100 ml base sol (2.4×10^{-4} M $AuCl_4^-$ + 1.6×10^{-3} M Citrate) at 65 °C

λ (nm)	0 hr	0.30 hr	0.75 hr	2.27 hr
490	0.548	0.542	0.544	0.523
500	0.629	0.626	0.628	0.602
510	0.707	0.707	0.710	0.681
520	0.748	0.753	0.754	0.726
525	0.744	0.750	0.751	0.726
530	0.723	0.730	0.730	0.708
540	0.637	0.640	0.640	0.628
550	0.519	0.517	0.515	0.513
560	0.407	0.402	0.400	0.406
570	0.320	0.315	0.312	0.324
580	0.256	0.253	0.249	0.265
590	0.203	0.202	0.198	0.218
600	0.166	0.167	0.164	0.185
610	0.131	0.135	0.131	0.155

Table 3

Reaction 3 Absorbance Data

15 ml of 2.4×10^{-4} M $AuCl_4^-$ added back to

100 ml base sol (2.4×10^{-4} M $AuCl_4^-$ + 1.6×10^{-3} M Citrate) at 65 ^{0}C

λ (nm)	0 hr	0.267 hr	0.72 hr	2.13 hr
490	0.548	0.559	0.560	0.535
500	0.629	0.644	0.646	0.615
510	0.707	0.728	0.730	0.694
520	0.748	0.773	0.777	0.738
525	0.744	0.769	0.774	0.737
530	0.723	0.746	0.753	0.718
540	0.637	0.651	0.660	0.634
550	0.519	0.523	0.532	0.518
560	0.407	0.407	0.415	0.412
570	0.320	0.319	0.327	0.331
580	0.256	0.257	0.265	0.274
590	0.203	0.207	0.214	0.229
600	0.166	0.173	0.180	0.197
610	0.131	0.140	0.148	0.167

Table 4

Reaction 4 Absorbance Data

20 ml of 2.4×10^{-4} M $AuCl_4^-$ added back to

100 ml base sol (2.4×10^{-4} M $AuCl_4^-$ + 1.6×10^{-3} M Citrate) at 65 °C

λ (nm)	0 hr	0.23 hr	0.683hr	2.17 hr
490	0.548	0.553	0.551	0.531
500	0.629	0.639	0.636	0.611
510	0.707	0.724	0.720	0.691
520	0.748	0.770	0.767	0.736
525	0.744	0.767	0.763	0.735
530	0.723	0.746	0.742	0.716
540	0.637	0.653	0.650	0.631
550	0.519	0.526	0.524	0.512
560	0.407	0.408	0.408	0.404
570	0.320	0.320	0.321	0.323
580	0.256	0.258	0.260	0.266
590	0.203	0.207	0.210	0.222
600	0.166	0.173	0.176	0.192
610	0.131	0.140	0.136 0	0.162

Table 5

Reaction 5 Absorbance Data

75 ml of 2.4×10^{-4} M $AuCl_4^-$ added back to

100 ml base sol (2.4×10^{-4} M $AuCl_4^-$ + 1.6×10^{-3} M Citrate) at 65 °C

λ (nm)	0 hr	0.217 hr	0.65 hr	2.17 hr	2.75 hr	3.02 hr
490	0.548	0.553	0.540	0.524	0.345	0.546
500	0.629	0.640	0.624	0.604	0.399	0.638
510	0.707	0.725	0.705	0.683	0.460	0.729
520	0.748	0.768	0.749	0.726	0.512	0.773
525	0.744	0.762	0.746	0.724	0.529	0.764
530	0.723	0.737	0.724	0.705	0.537	0.732
540	0.637	0.638	0.634	0.622	0.529	0.620
550	0.519	0.508	0.513	0.510	0.492	0.486
560	0.407	0.391	0.404	0.410	0.441	0.375
570	0.320	0.304	0.324	0.336	0.387	0.300
580	0.256	0.243	0.268	0.286	0.336	0.251
590	0.203	0.194	0.222	0.245	0.283	0.212
600	0.166	0.161	0.190	0.216	0.241	0.187
610	0.131	0.129	0.161	0.187	0.200	0.161

Table 6

Reaction 6 Absorbance Data

50 ml of 2.4 x 10^{-4} M $AuCl_4^-$ added back to

100 ml base sol (2.4 x 10^{-4} M $AuCl_4^-$ + 1.6 x 10^{-3} M Citrate) at 65 °C

Lambda (nm)	Base Sol	0.267 Hours
490	0.548	0.271
500	0.629	0.298
510	0.707	0.325
520	0.748	0.344
525	0.744	0.349
530	0.723	0.351
540	0.637	0.351
550	0.519	0.352
560	0.407	0.363
570	0.320	0.377
580	0.256	0.393
590	0.203	0.400
600	0.166	0.408
610	0.131	0.408
620		0.404
630		0.398
640		0.391
650		0.384

Table 7

Reaction 7.1 Absorbance Data

40 ml of 2.4×10^{-4} M $AuCl_4^-$ added back to

100 ml base sol (2.4×10^{-4} M $AuCl_4^-$ + 1.6×10^{-3} M Citrate) at 65 °C

λ (nm)	0 min.	4.5 min.	10 min.	14.8 min.	24 m	70 m
490	0.542	0.559	0.359	0.360	0.362	0.381
500	0.620	0.648	0.413	0.414	0.415	0.436
510	0.696	0.736	0.471	0.472	0.474	0.495
520	0.738	0.789	0.519	0.522	0.524	0.546
525	0.737	0.789	0.535	0.537	0.539	0.562
530	0.719	0.770	0.542	0.545	0.548	0.571
540	0.641	0.680	0.533	0.535	0.540	0.564
550	0.530	0.550	0.495	0.497	0.502	0.528
560	0.424	0.426	0.444	0.445	0.452	0.477
570	0.340	0.332	0.388	0.390	0.396	0.421
580	0.278	0.265	0.336	0.337	0.344	0.367
590	0.222	0.210	0.280	0.281	0.288	0.305
600	0.190	0.176	0.240	0.240	0.246	0.266
610	0.158	0.142	0.197	0.198	0.203	0.220

Table 8

Reaction 7.1 Peak Absorbance Data

40 ml of 2.4×10^{-4} M $AuCl_4^-$ added back to

100 ml base sol (2.4×10^{-4} M $AuCl_4^-$ + 1.6×10^{-3} M Citrate) at 65 °C

Time (min.)	λ_{max} (nm)
0.00	522.9
4.50	522.8
24.00	533.3
70.00	533.0

Table 9

Reaction 7.2 Absorbance Data

40 ml of 2.4 x 10^{-4} M $AuCl_4^-$ added back to

100 ml base sol (2.4×10^{-4} M $AuCl_4^-$ + 1.6×10^{-3} M Citrate) at 65 °C

λ (nm)	0 hr	23 hr
500	0.644	0.658
510	0.725	0.748
520	0.777	0.790
530	0.768	0.746
540	0.693	0.628
550	0.573	0.486
560	0.459	0.366
570	0.361	0.282
580	0.287	0.226
590	0.230	0.185
600	0.184	0.151

Table 10

Reaction 7.2 Raw Absorbance Peak Data

40 ml of 2.4 x 10^{-4} M $AuCl_4^-$ added back to

100 ml base sol (2.4 x 10^{-4} M $AuCl_4^-$ + 1.6 x 10^{-3} M Citrate) at 65 °C

Time (hours)	λ_{max} (nm)
0.000	524.4
0.017	532.8
0.167	533.1
0.500	533.4
1.033	533.2
2.067	531.6
4.800	521.9
9.883	522.0
13.000	521.3
22.750	521.7

Table 11

Reaction 8 Peak Absorbance Data

50 ml of 2.4×10^{-4} M $AuCl_4^-$ added back to

100 ml base sol (2.4×10^{-4} M $AuCl_4^-$ + 1.6×10^{-3} M Citrate) at 65 °C

Time (hours)	λ_{max} (nm)
0.00	523.5
0.02	533.1
0.18	533.6
0.50	533.2
1.00	533.6
2.00	532.6
4.80	521.2
9.13	521.0
12.87	520.0

Table 12

Reaction 9 Peak Absorbance Data

60 ml of 2.4 x 10^{-4} M $AuCl_4^-$ added back to

100 ml base sol (2.4 x 10^{-4} M $AuCl_4^-$ + 1.6 x 10^{-3} M Citrate) at 65 °C

Time (Hours)	λ_{max} (nm)
0.00	524.4
0.02	533.0
0.17	534.2
0.50	534.1
1.07	534.8
2.07	533.6
4.67	525.2
9.08	521.1
11.33	521.3
12.78	521.1
23.00	520.8

Table 13

Reaction 10 Peak Absorbance Data

70 ml of 2.4 x 10^{-4} M $AuCl_4^-$ added back to

100 ml base sol (2.4 x 10^{-4} M $AuCl_4^-$ + 1.6 x 10^{-3} M Citrate) at 65 °C

Time (Hours)	λ_{max} (nm)
0.00	523.5
0.02	534.0
0.17	534.2
0.50	534.4
1.00	534.8
2.00	535.5
4.28	524.9
9.28	521.0
9.83	520.7
11.75	520.3
12.13	520.0
12.73	521.1

Table 14

Reaction 11.1 Peak Absorbance Data

80 ml of 2.4 x 10^{-4} M $AuCl_4^-$ added back to

100 ml base sol (2.4 x 10^{-4} M $AuCl_4^-$ + 1.6 x 10^{-3} M Citrate) at 65 °C

Time (Hours)	λ_{max} (nm)
0.00	524.0
0.05	534.0
0.17	534.2
0.50	534.1
1.00	534.6
2.00	536.0
4.00	525.2
9.60	520.7
10.90	520.5
12.00	521.0

Table 15

Reaction 11.2 Absorbance Data

80 ml of 2.4 x 10^{-4} M $AuCl_4^-$ added back to

100 ml base sol (2.4 x 10^{-4} M $AuCl_4^-$ + 1.6 x 10^{-3} M Citrate) at 65 °C

	Time (hours)										
λ (nm)	0	0.20	0.48	0.73	1.03	1.53	2.2	2.7	2.9	3.13	12.87
500	0.637	0.305	0.332	0.354	0.382	0.427	0.525	0.605	0.618	0.634	0.655
510	0.715	0.349	0.384	0.404	0.437	0.485	0.599	0.695	0.705	0.721	0.742
520	0.763	0.390	0.424	0.448	0.480	0.537	0.657	0.747	0.762	0.775	0.782
530	0.751	0.411	0.447	0.474	0.510	0.568	0.683	0.742	0.756	0.757	0.735
540	0.678	0.408	0.445	0.476	0.512	0.571	0.665	0.667	0.679	0.669	0.620
550	0.565	0.380	0.422	0.454	0.493	0.548	0.608	0.555	0.562	0.530	0.478
560	0.451	0.344	0.386	0.420	0.458	0.508	0.533	0.443	0.448	0.423	0.364
570	0.357	0.307	0.349	0.383	0.419	0.462	0.455	0.350	0.353	0.330	0.283
580	.283	0.268	0.307	0.340	0.377	0.409	0.384	0.282	0.281	0.265	0.226
590	0.230	0.231	0.269	0.300	0.330	0.353	0.320	0.227	0.232	0.215	0.186
600	0.184	0.194	0.229	0.258	0.285	0.306	0.268	0.187	0.188	0.174	0.152

Table 16

Reaction 11.2 Peak Absorbance Data

80 ml of 2.4×10^{-4} M $AuCl_4^-$ added back to

100 ml base sol (2.4×10^{-4} M $AuCl_4^-$ + 1.6×10^{-3} M Citrate) at 65 °C

Time (hours)	λ_{max} (nm)
0.000	524.0
0.017	534.0
0.200	534.1
0.483	535.2
0.733	535.8
1.033	536.6
1.533	536.4
2.200	531.5
2.700	524.7
2.900	524.0
3.133	522.8
12.87	520.3

Figure 1
Reaction 1 Absorbance Curve

5 ml of 2.4×10^{-4} M $AuCl_4^-$ added back
to 100 ml base sol (2.4×10^{-4} M $AuCl_4^-$ + 1.6×10^{-3} M Citrate) at 65 °C

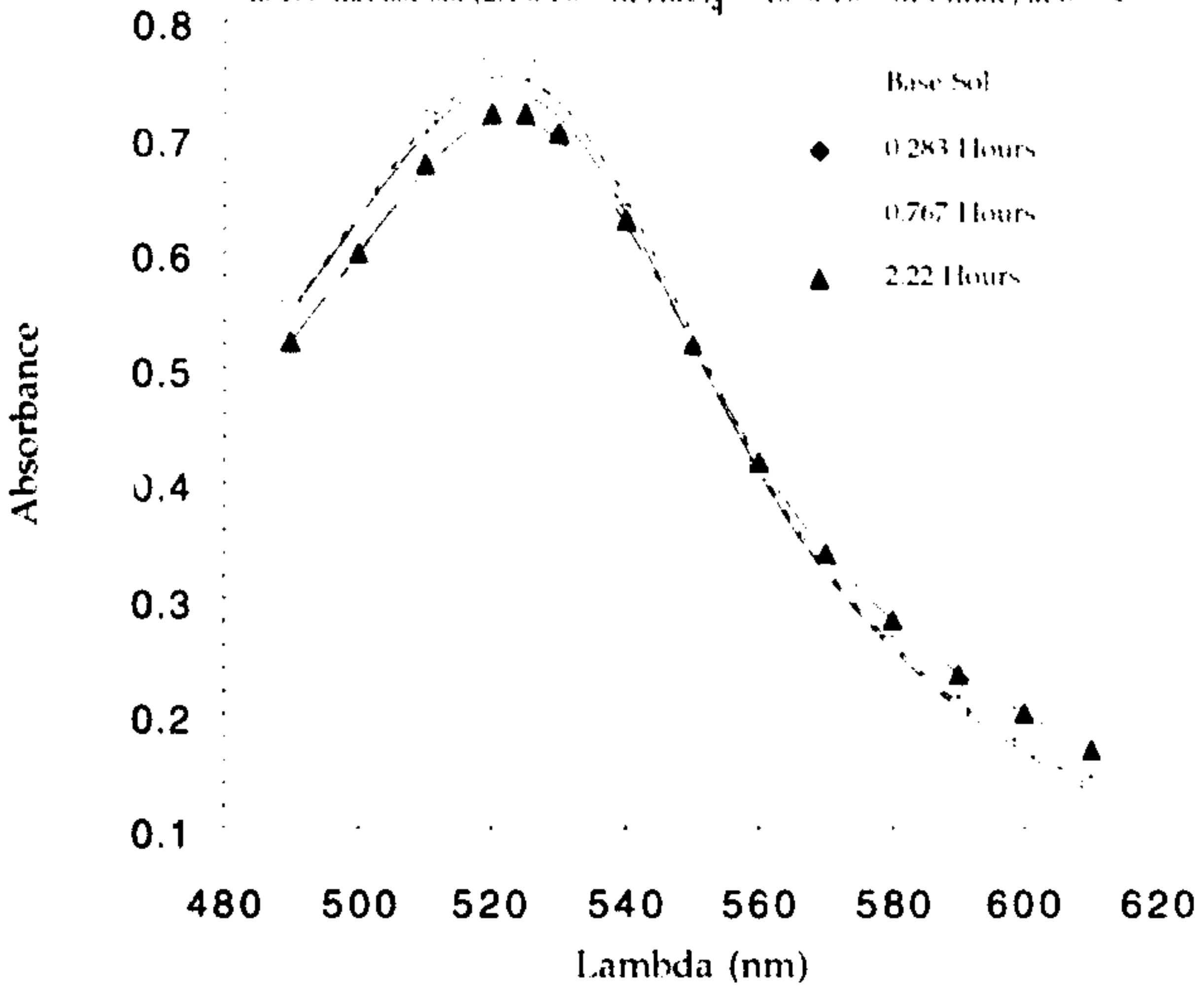


Figure 2
Reaction 1 Absorbance Curve

5 ml of 2.4×10^{-4} M $AuCl_4^-$ added back
to 100 ml base sol (2.4×10^{-4} M $AuCl_4^-$ + 1.6×10^{-3} M Citrate) at 65 °C

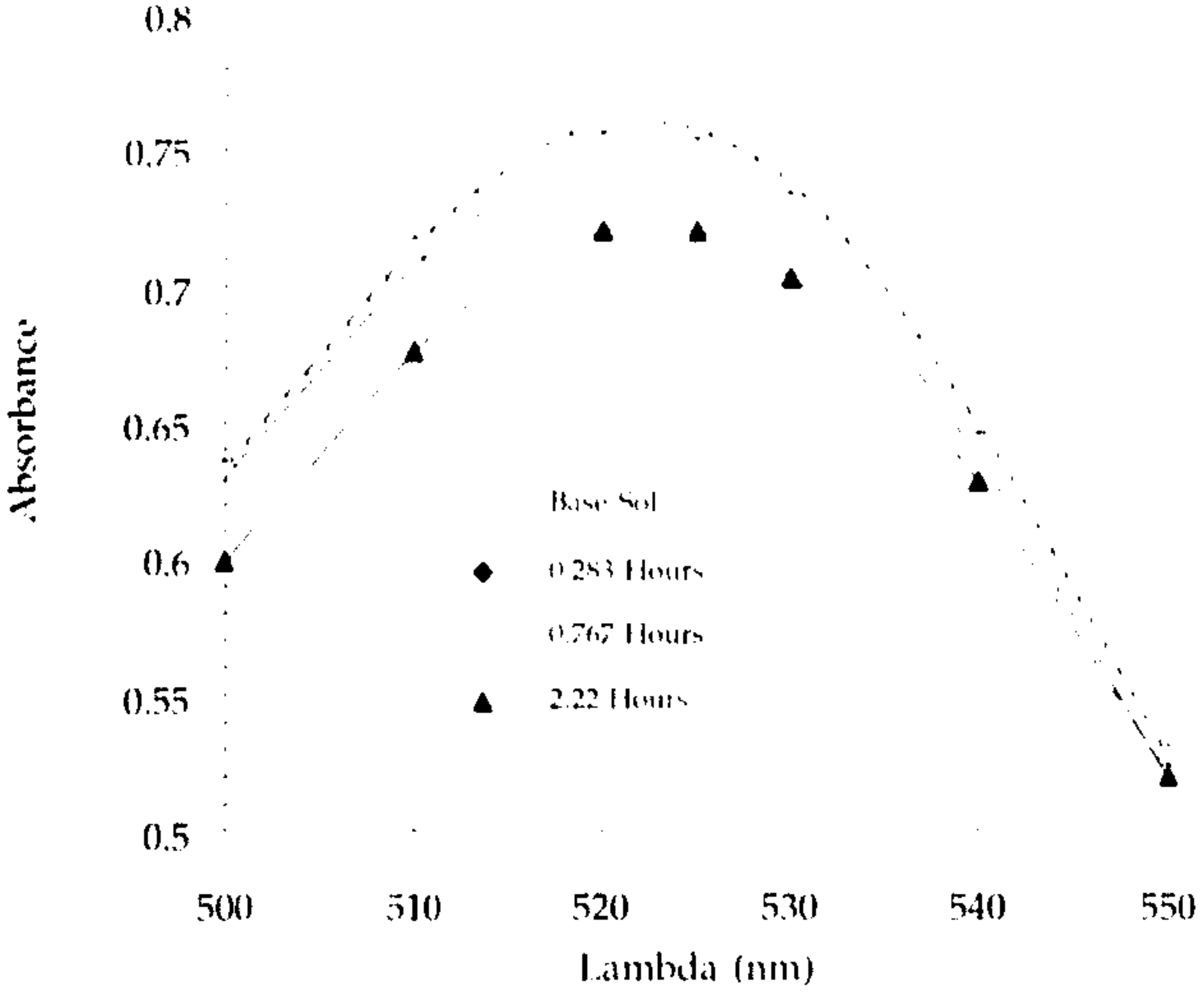


Figure Three
Reaction 2 Absorbance Data

10 ml of 2.4 x 10^{-4} M $AuCl_4^-$ added back
to 100 ml base sol (2.4 x 10^{-4} M $AuCl_4^-$ + 1.6 x 10^{-3} M Citrate) at 65 °C

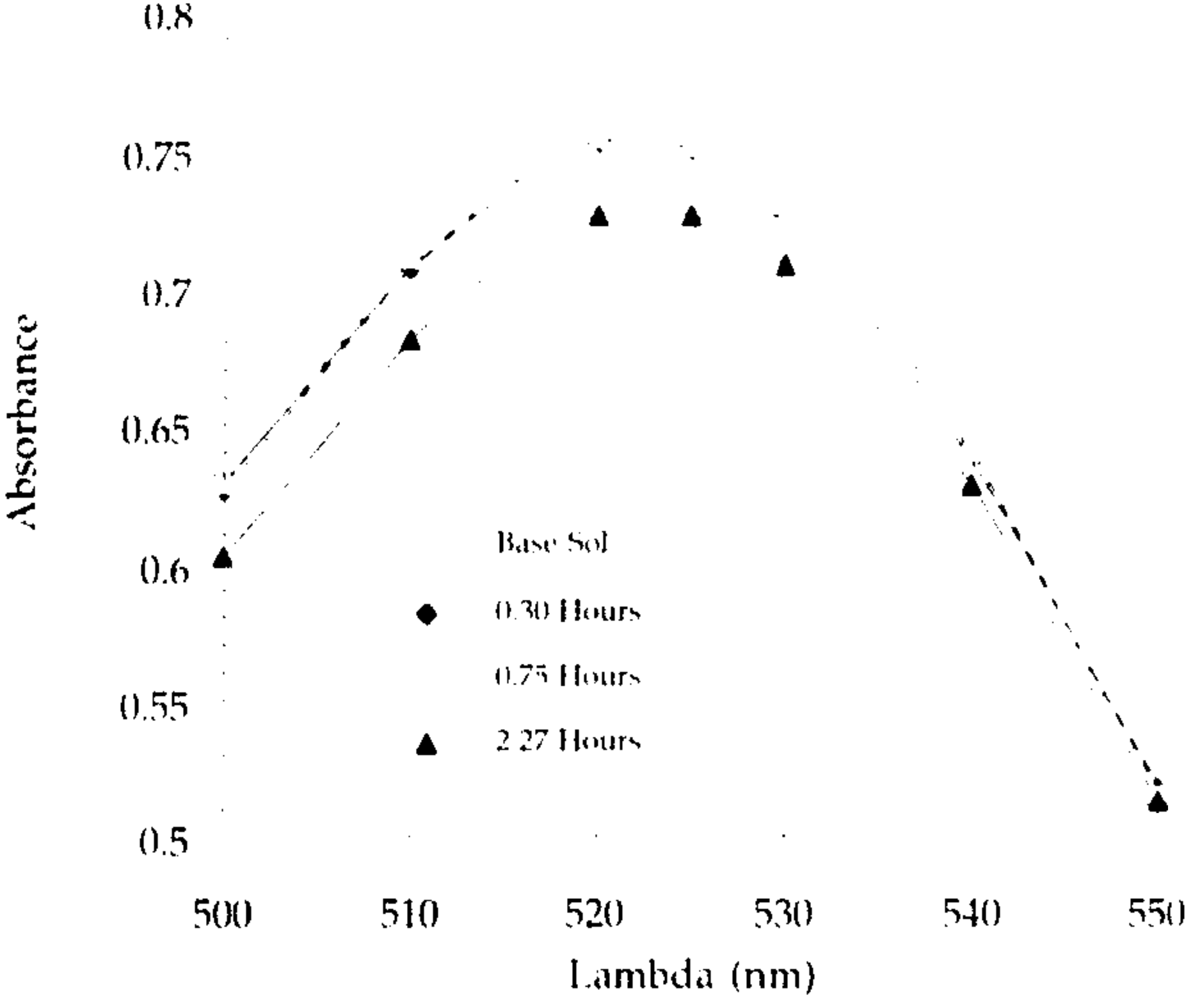


Figure 4
Reaction 3 Absorbance Curve

15 ml of 2.4×10^{-4} M $AuCl_4^-$ added back
to 100 ml base sol (2.4×10^{-4} M $AuCl_4^-$ + 1.6×10^{-3} M Citrate) at 65 °C

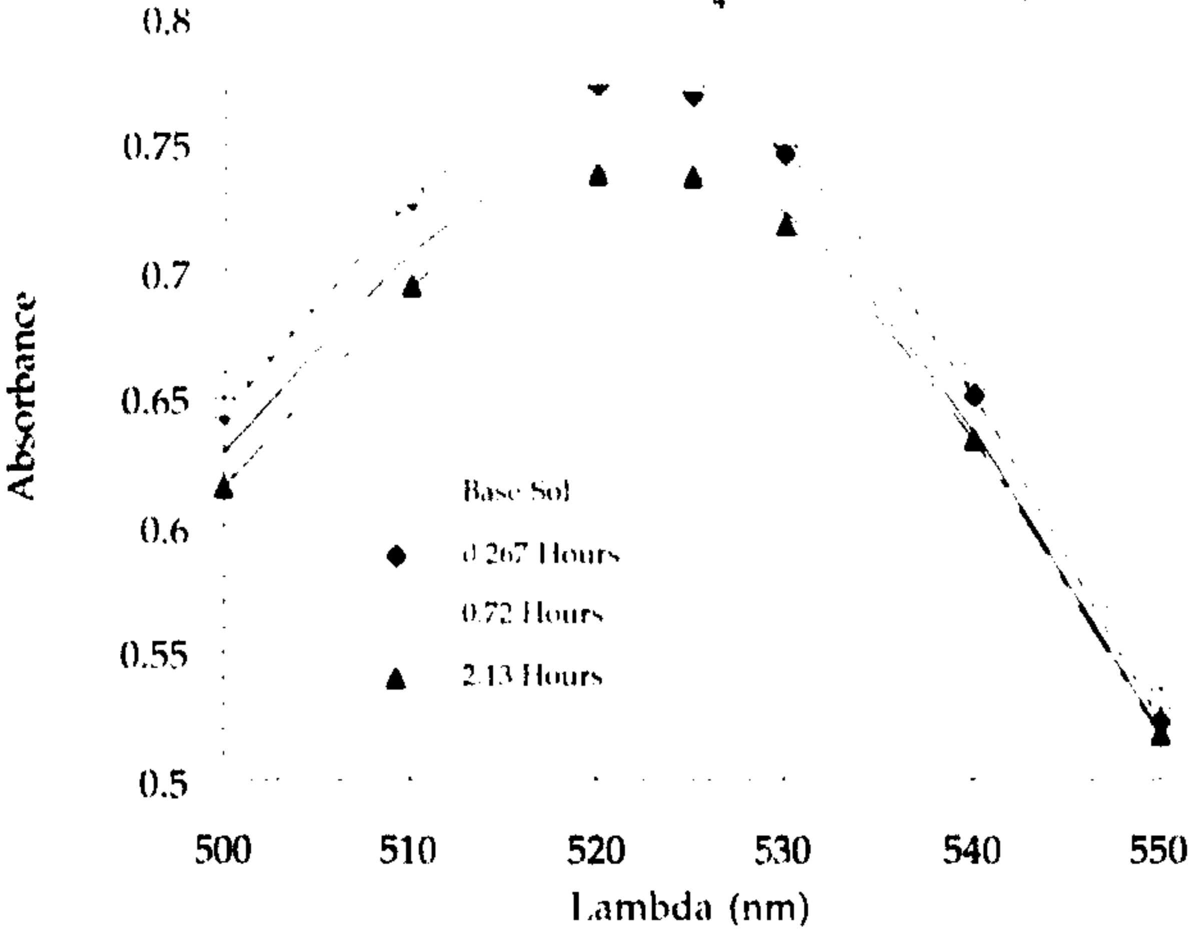


Figure 5
Reaction 4 Absorbance Curve

20 ml of 2.4 x 10^{-4} M $AuCl_4^-$ added back
to 100 ml base sol (2.4 x 10^{-4} M $AuCl_4^-$ + 1.6 x 10^{-3} M Citrate) at 65 °C

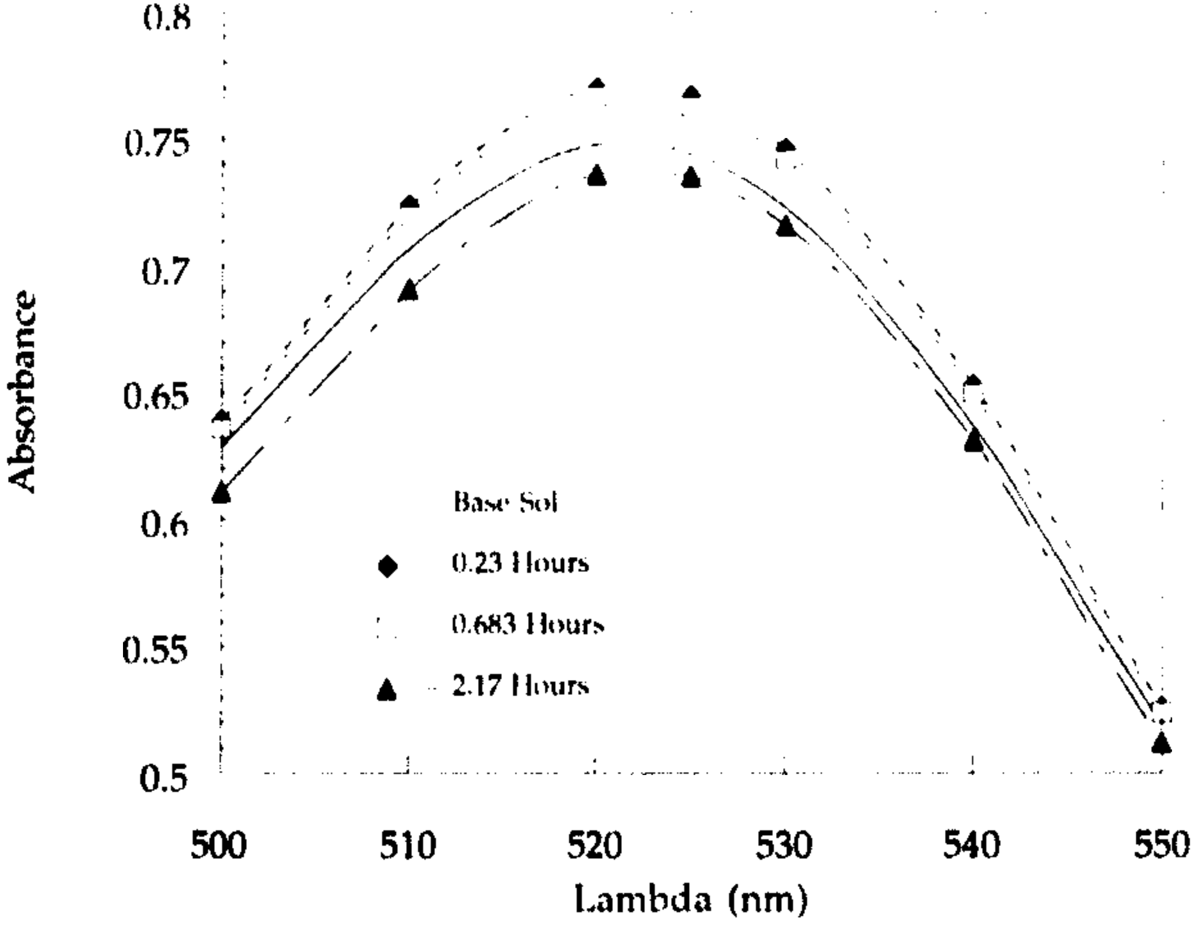


Figure 6
Reaction 5 Absorbance Curve

75 ml of 2.4×10^{-4} M $AuCl_4^-$ added back

to 100 ml base sol (2.4×10^{-4} M $AuCl_4^-$ + 1.6×10^{-3} M Citrate) at 65 °C

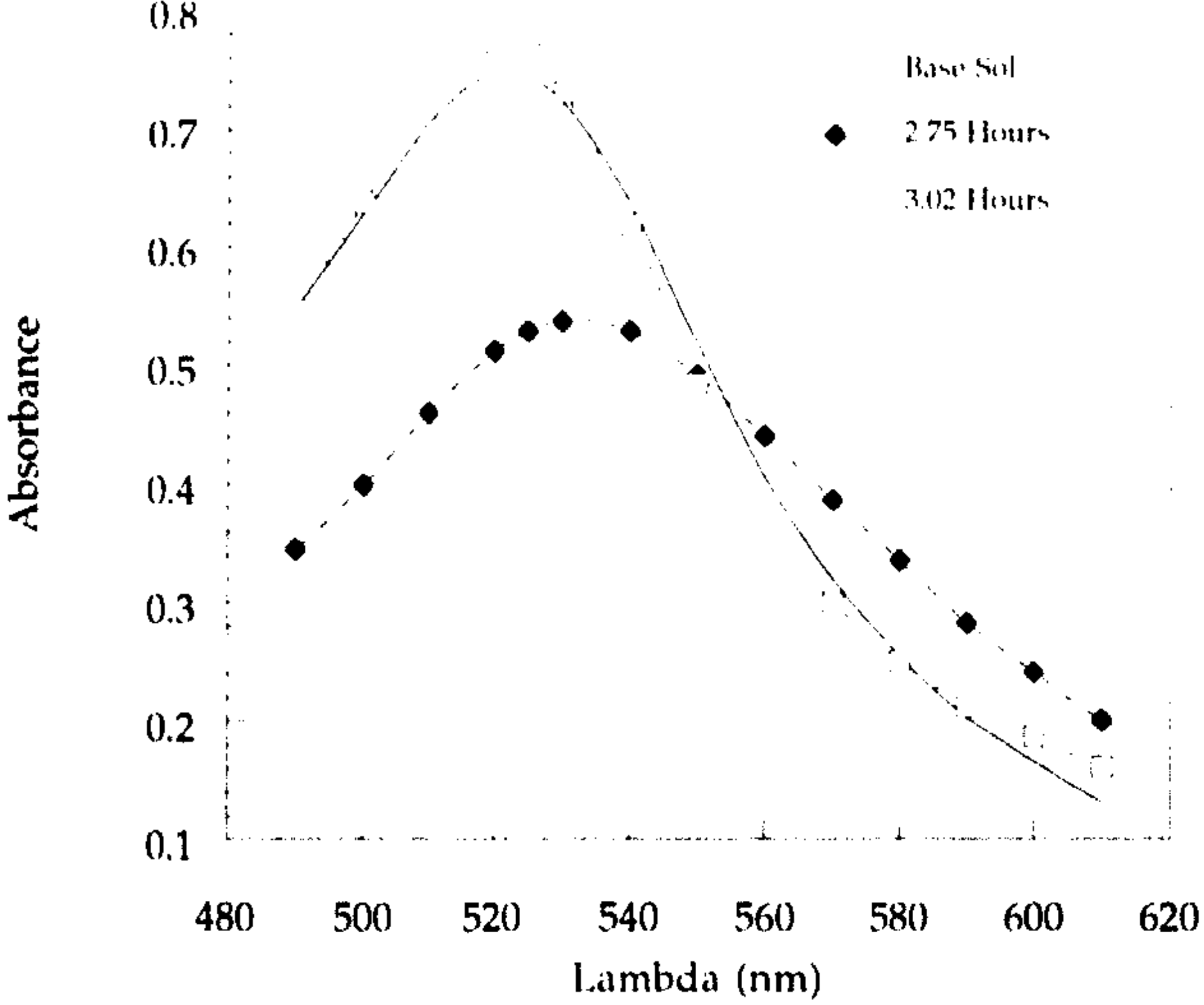


Figure 7
Reaction 6 Absorbance Curve

50 ml of 2.4×10^{-4} M $AuCl_4^-$ added back
to 100 ml base sol (2.4×10^{-4} M $AuCl_4^-$ + 1.6×10^{-3} M Citrate) at 65 °C

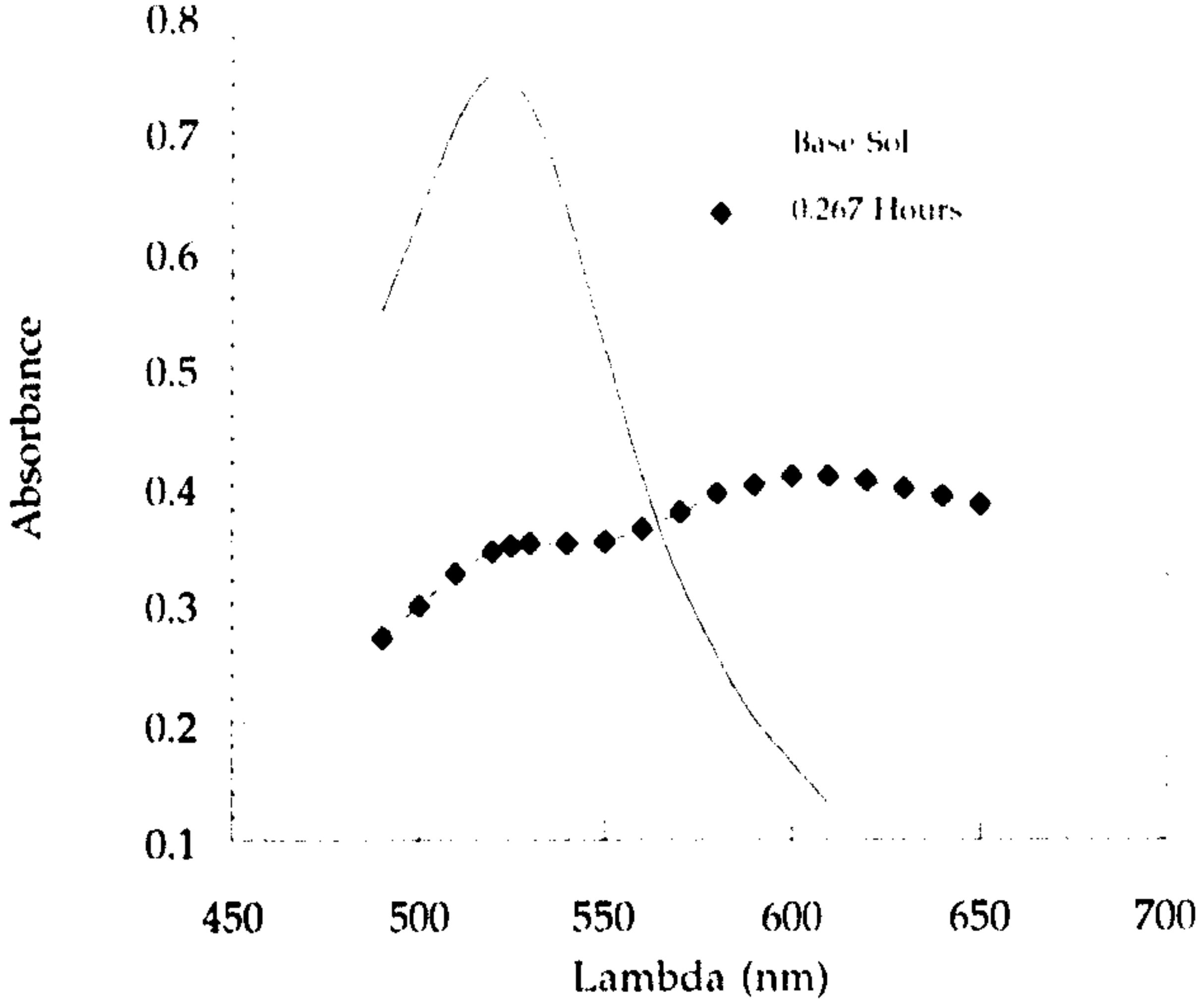


Figure 8

Reaction 7.1 Absorbance over Time

40 ml of 2.4 x 10^{-4} M $AuCl_4^-$ added back

to 100 ml base sol (2.4 x 10^{-4} M $AuCl_4^-$ + 1.6 x 10^{-3} M Citrate) at 65 °C

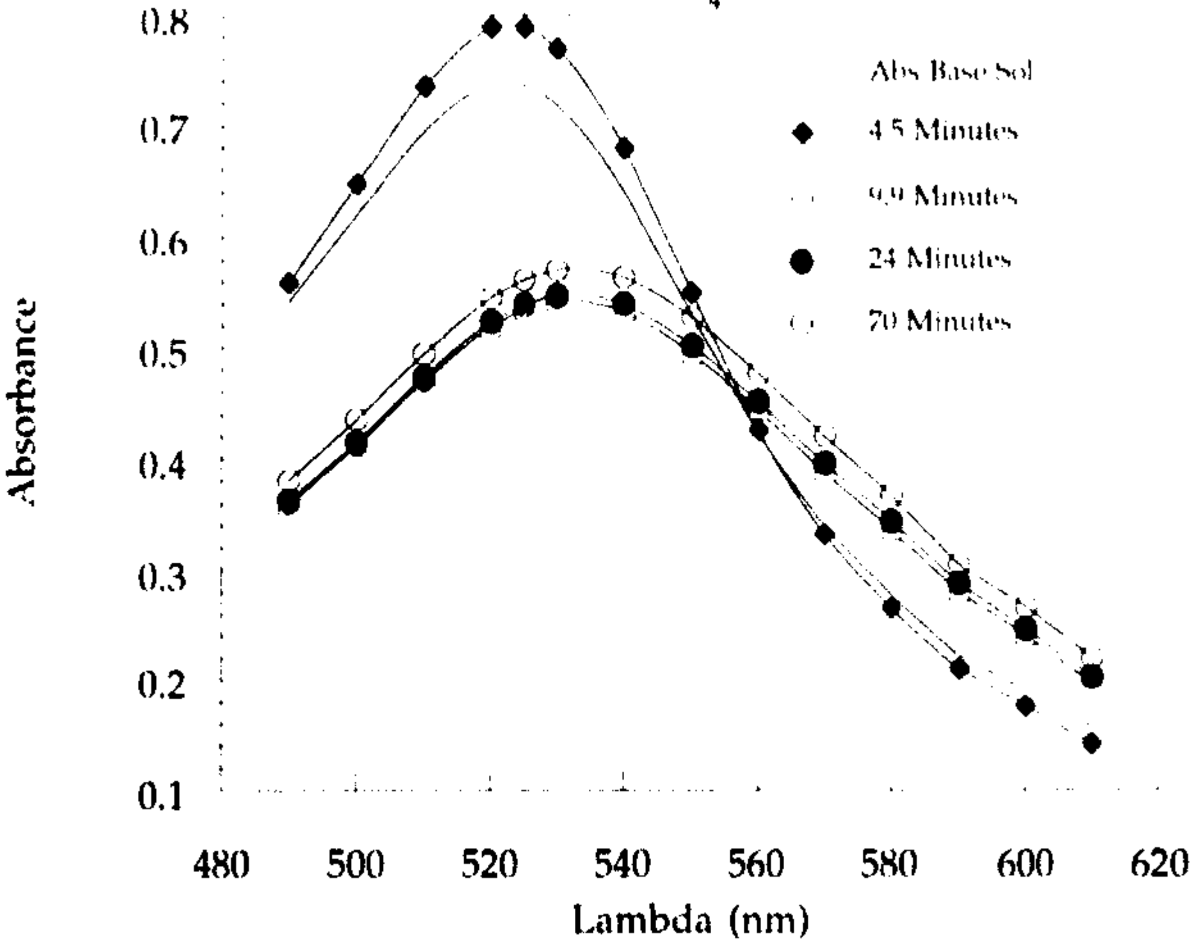


Figure 9
Reaction 7.1 Absorbance over Time

40 ml of 2.4×10^{-4} M $AuCl_4^-$ added back
to 100 ml base sol (2.4×10^{-4} M $AuCl_4^-$ + 1.6×10^{-3} M Citrate) at 65 °C

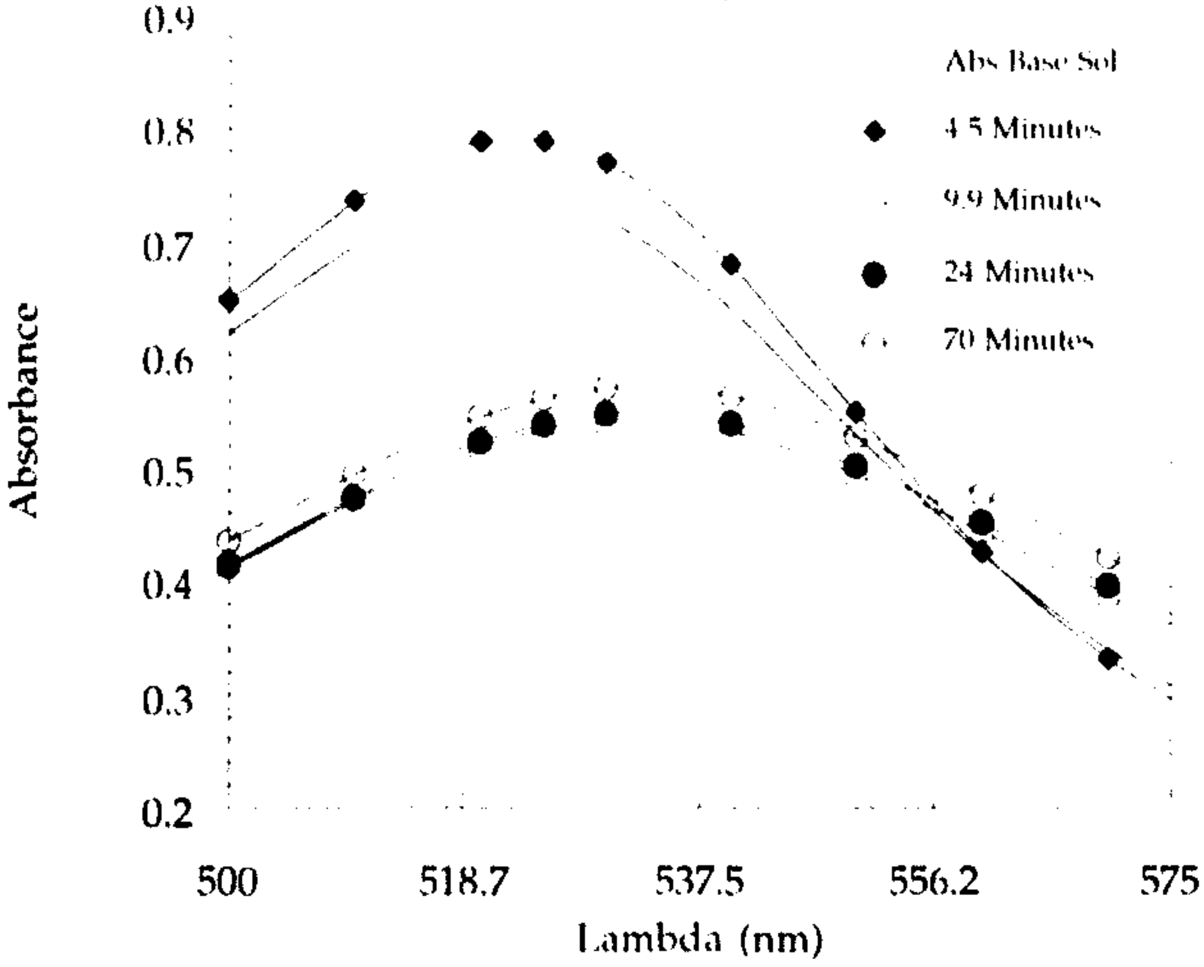


Figure 10

Reaction 7.2 Absorbance over Time

40 ml of 2.4×10^{-4} M $AuCl_4^-$ added back

to 100 ml base sol (2.4×10^{-4} M $AuCl_4^-$ + 1.6×10^{-3} M Citrate) at 65 °C

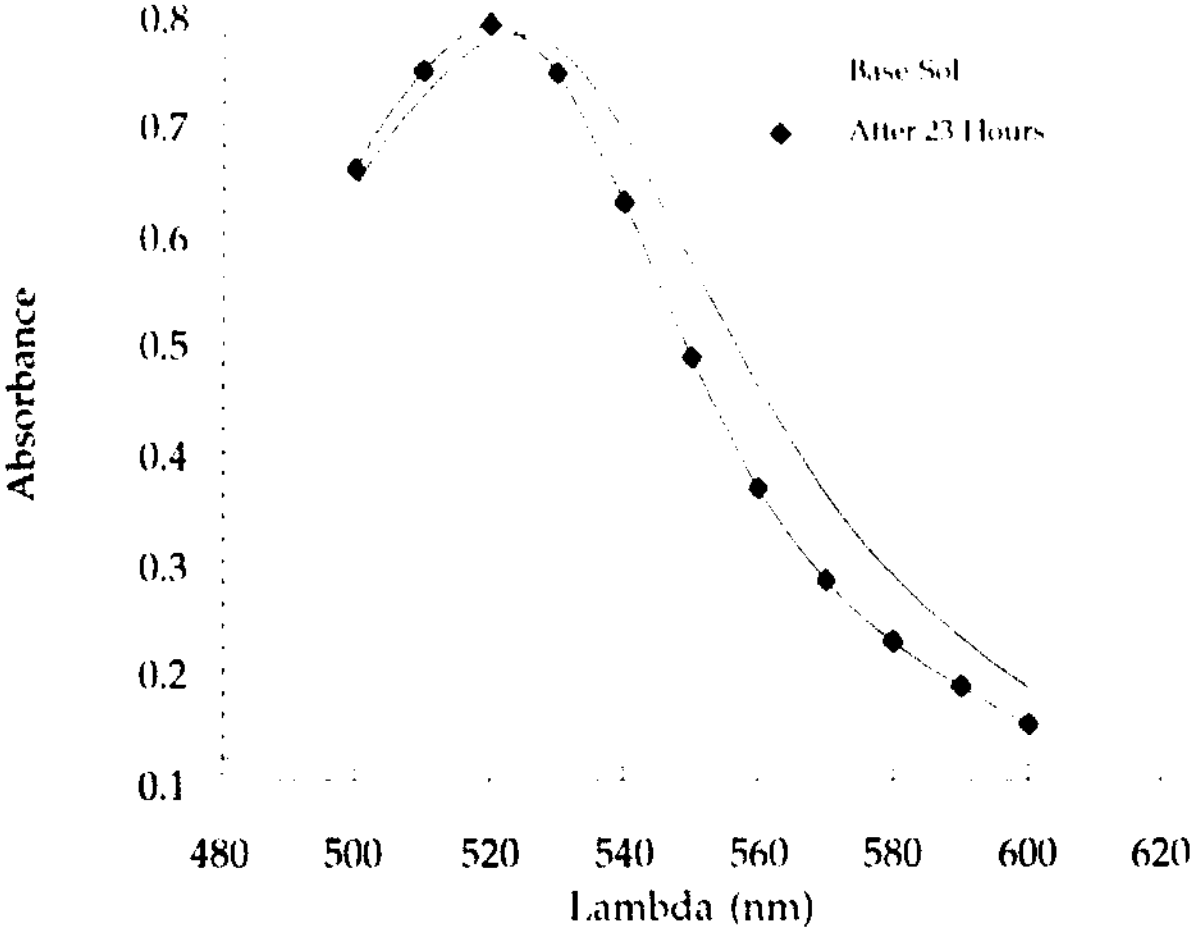


Figure 11

Reaction 7.2 Peak Absorbance vs. Time

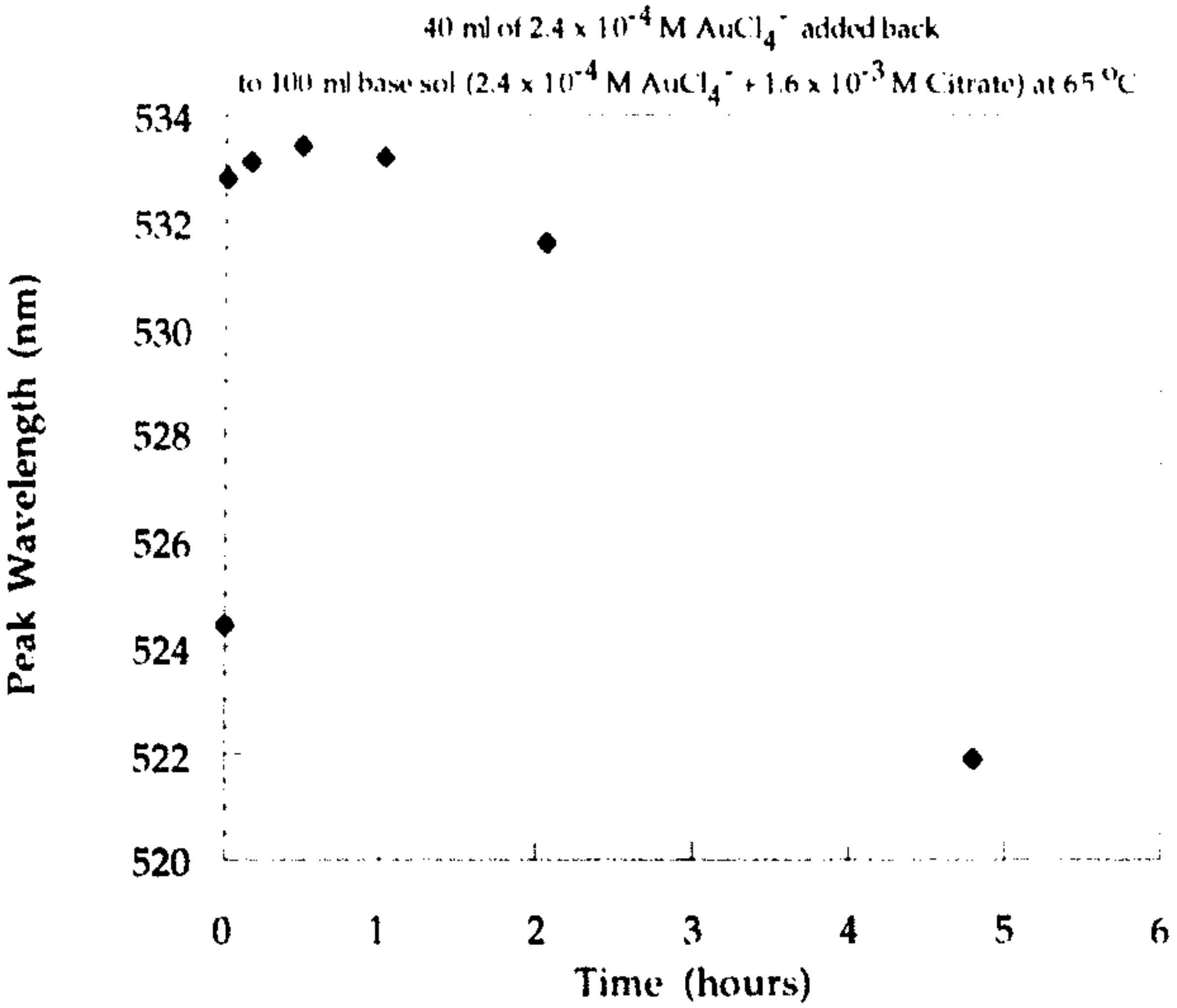


Figure 12
Reaction 8.1 Peak Absorbance vs. Time

50 ml of 2.4 x 10^{-4} M $AuCl_4^-$ added back
to 100 ml base sol (2.4 x 10^{-4} M $AuCl_4^-$ + 1.6 x 10^{-3} M Citrate) at 65 °C

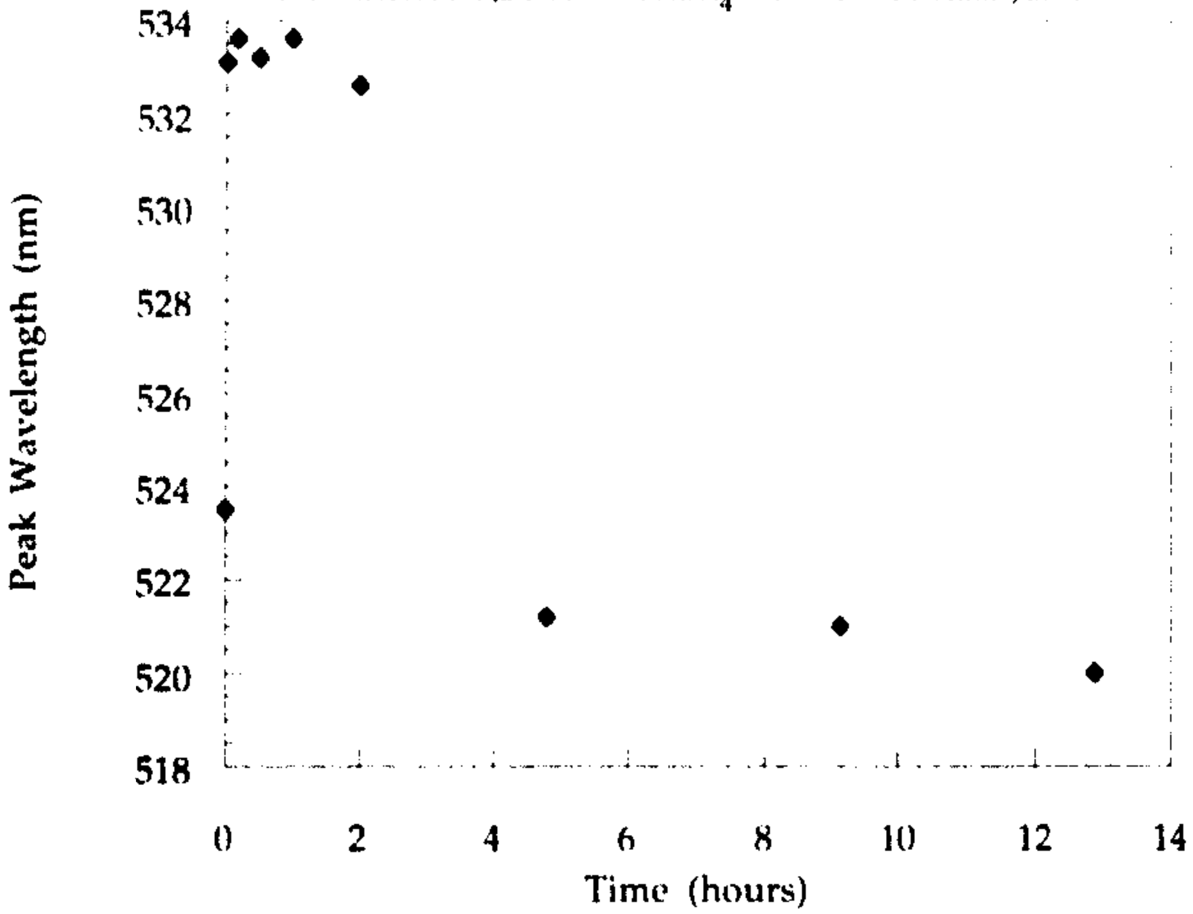


Figure 13
Reaction 9 Peak Absorbance vs. Time

60 ml of 2.4×10^{-4} M $AuCl_4^-$ added back
to 100 ml base sol (2.4×10^{-4} M $AuCl_4^-$ + 1.6×10^{-3} M Citrate) at 63°C

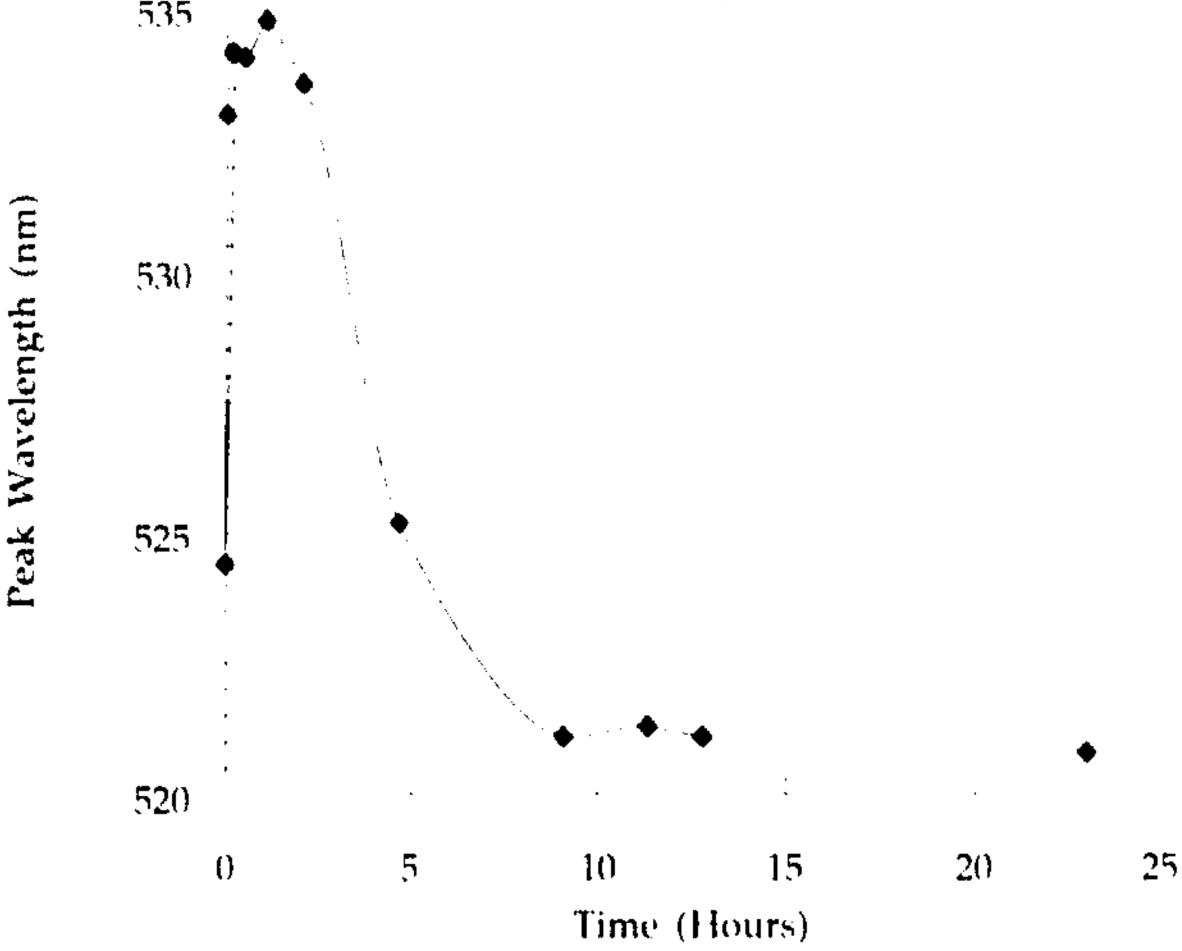


Figure 14
Reaction 10 Peak Absorbance vs. Time

70 ml of 2.4×10^{-4} M $AuCl_4^-$ added back
to 100 ml base sol (2.4×10^{-4} M $AuCl_4^-$ + 1.6×10^{-3} M Citrate) at 65 °C

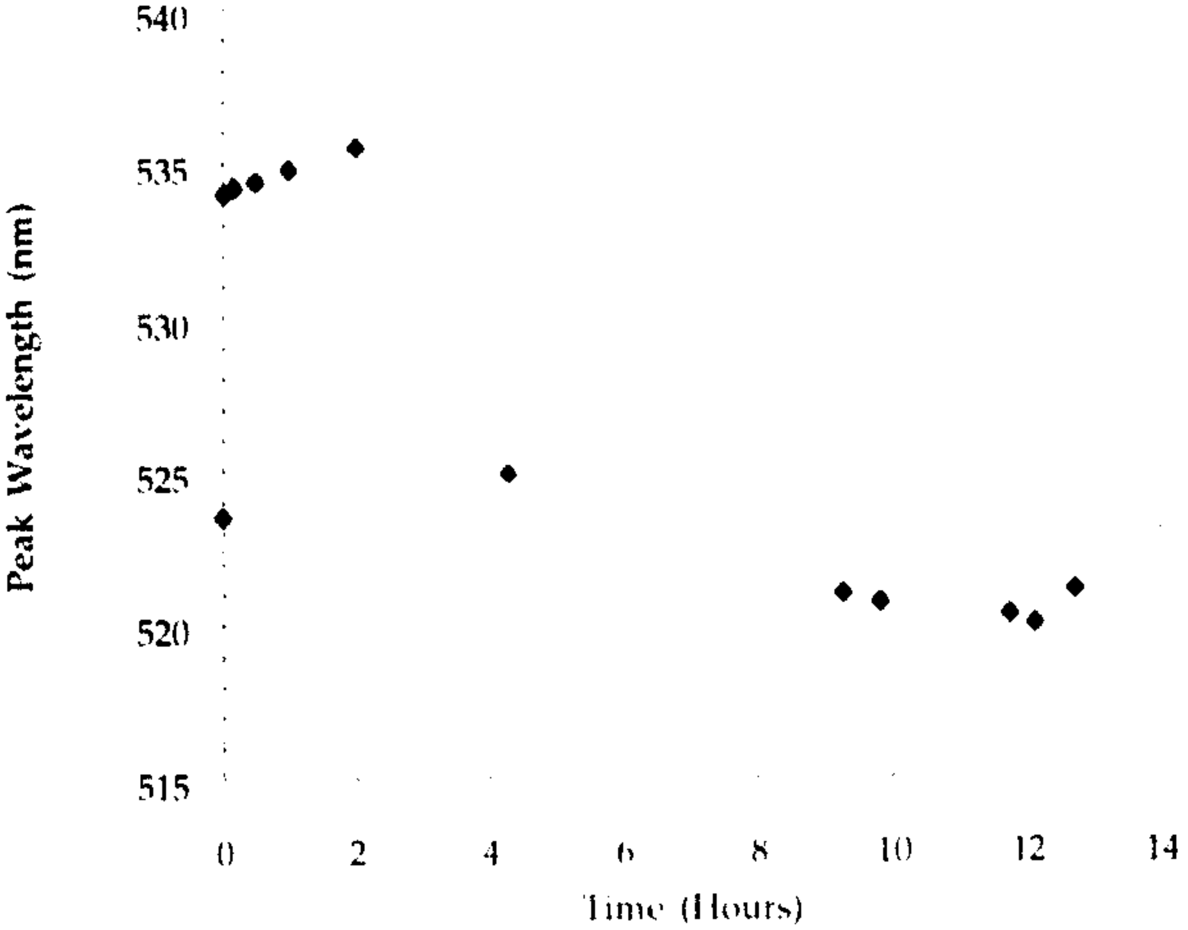


Figure 15
Reaction 11.1 Peak Absorbance vs. Time
80 ml of 2.4×10^{-4} M $AuCl_4^-$ added back
to 100 ml base sol (2.4×10^{-4} M $AuCl_4^-$ + 1.6×10^{-3} M Citrate) at 65°C

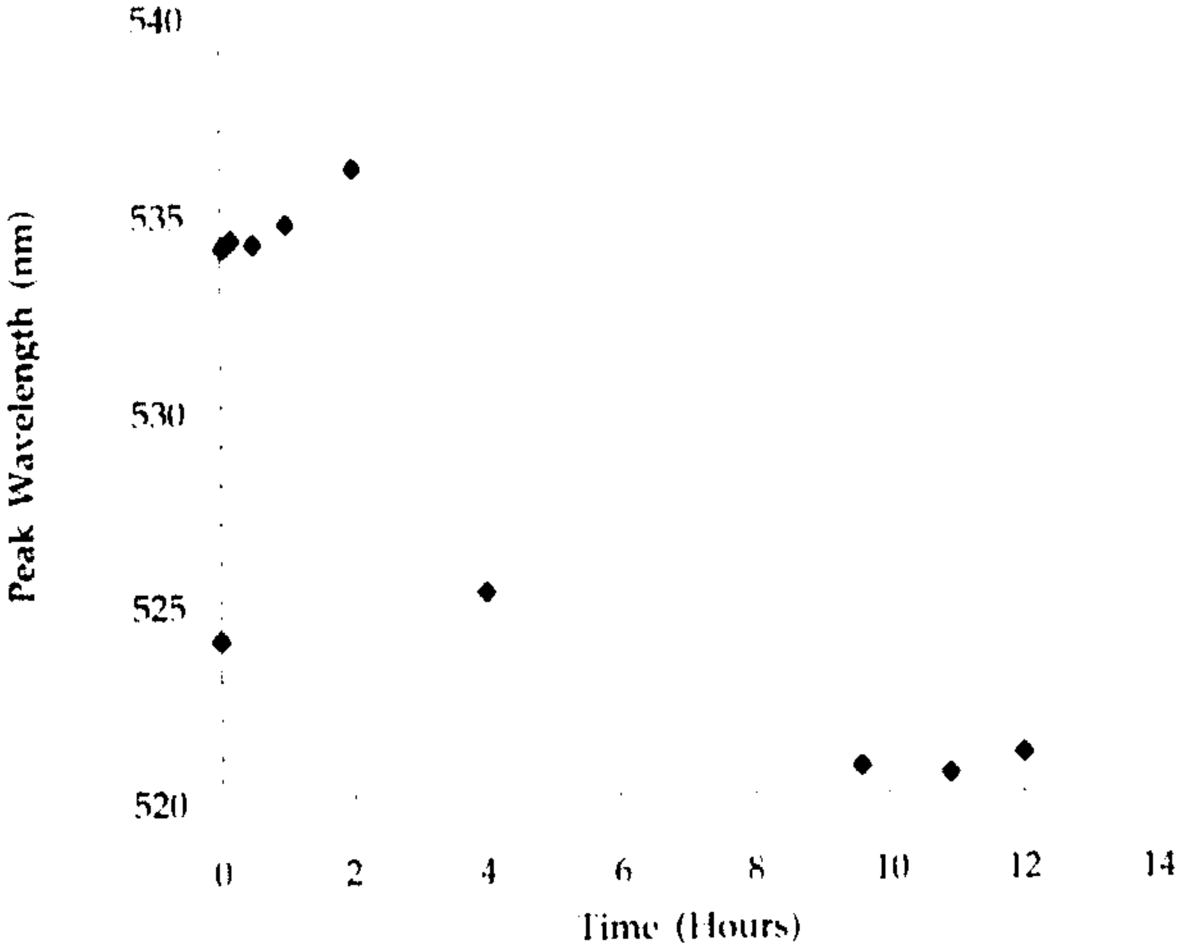


Figure 16
Reaction 11.2 Absorbance vs. Time

80 ml of 2.4×10^{-4} M $AuCl_4^-$ added back

to 100 ml base sol (2.4×10^{-4} M $AuCl_4^-$ + 1.6×10^{-3} M Citrate) at 65 °C

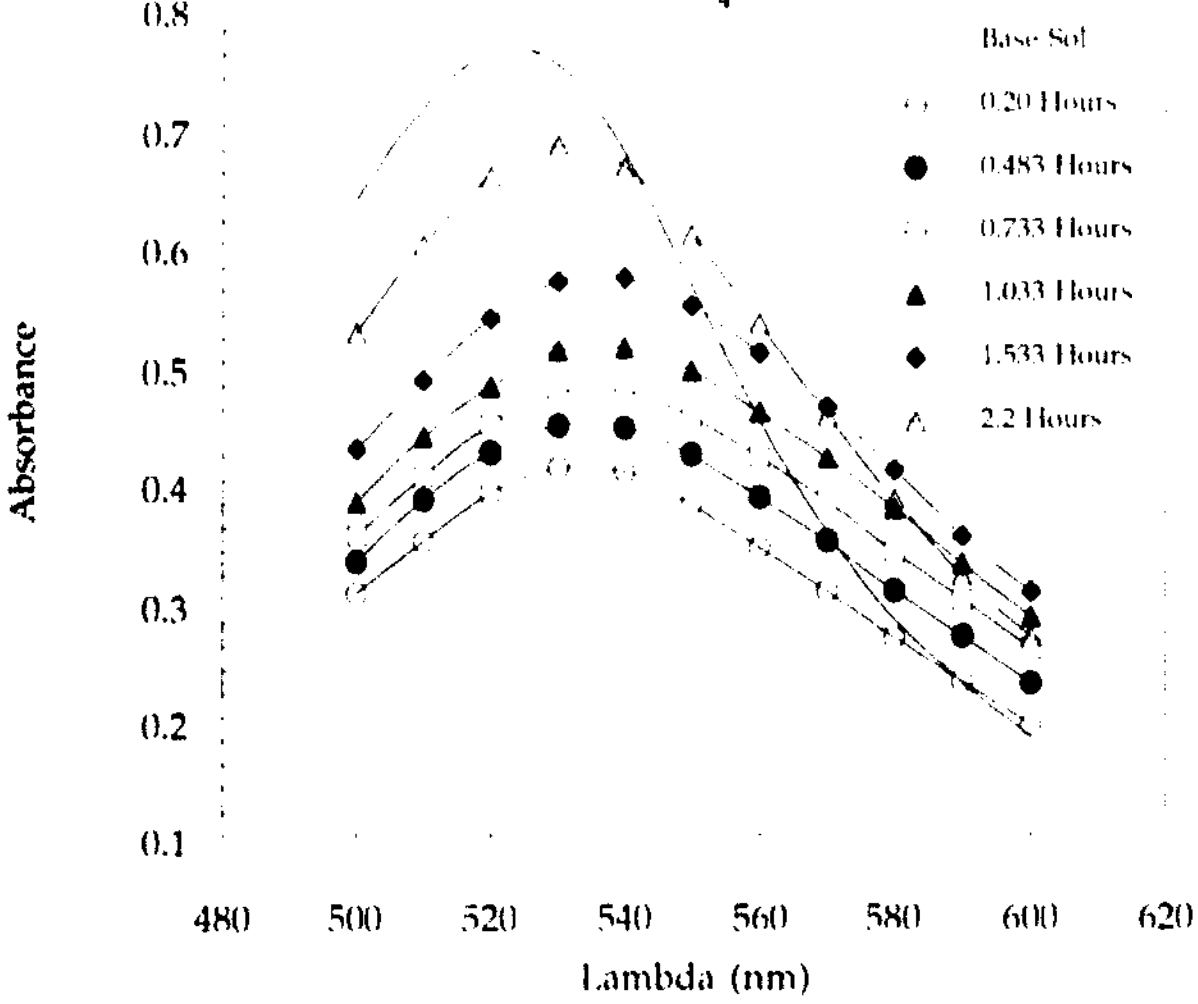
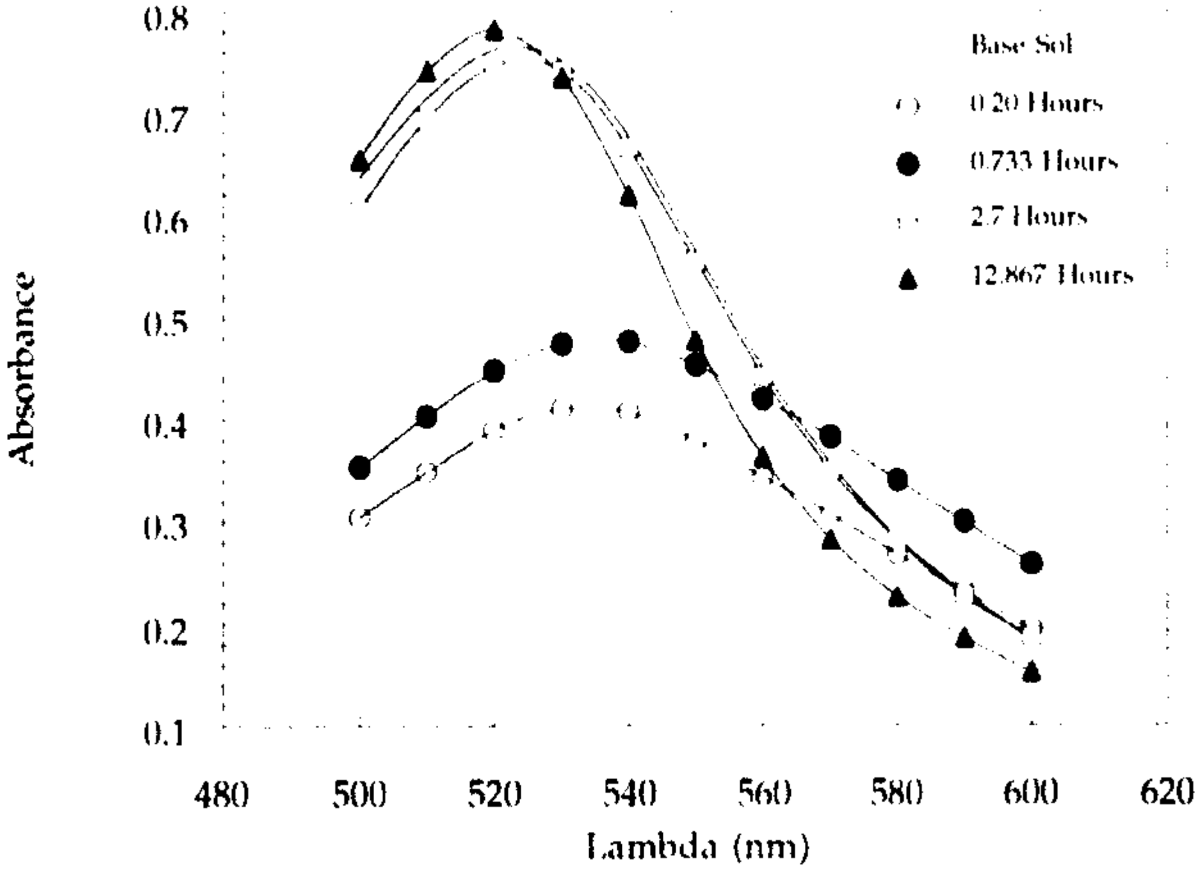


Figure 17
Reaction 11.2 Absorbance vs. Time, Graph 2

80 ml of 2.4 x 10^{-4} M $AuCl_4^-$ added back
to 100 ml base sol (2.4 x 10^{-4} M $AuCl_4^-$ + 1.6 x 10^{-3} M Citrate) at 65 °C



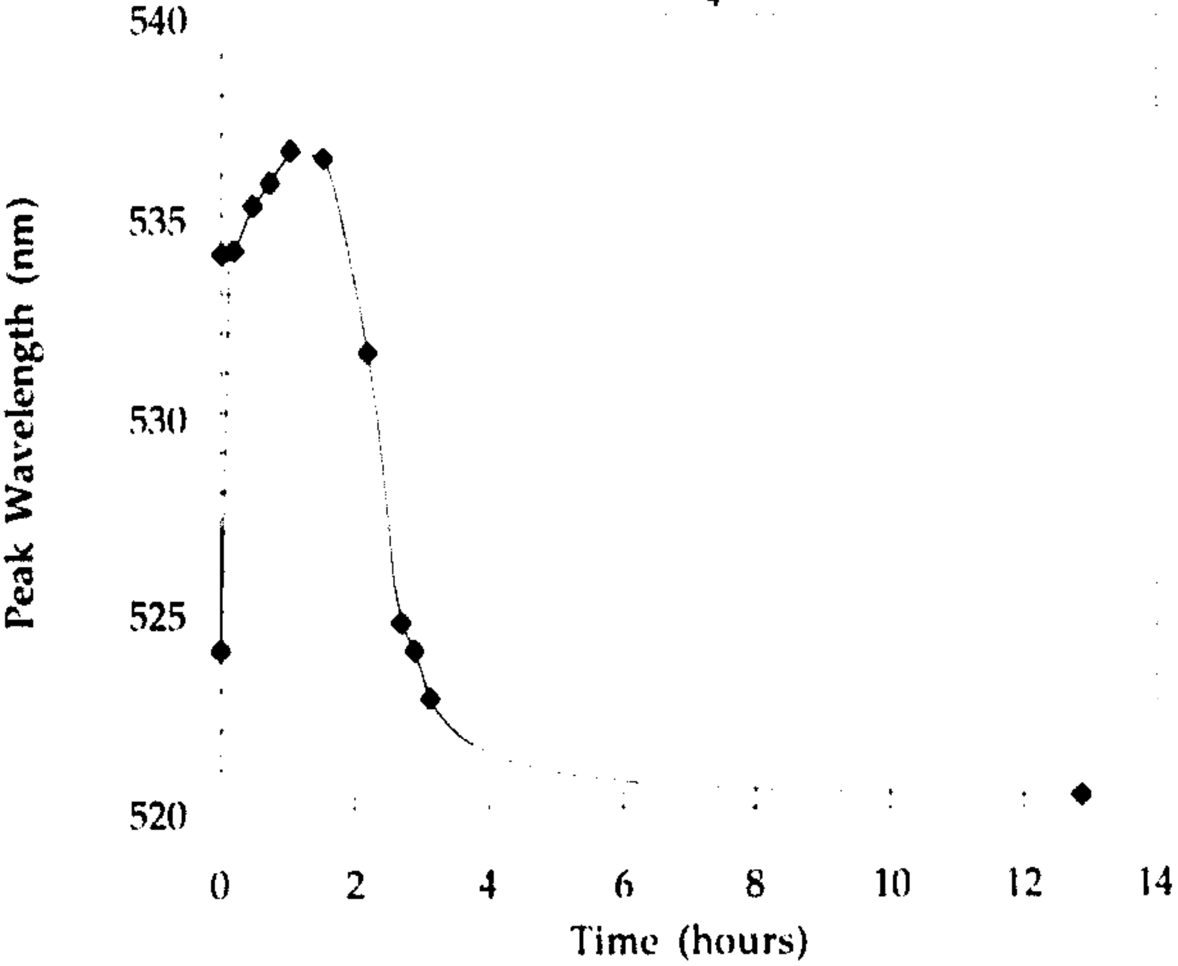


Figure 18
Reaction 11.2 Peak Absorbance vs. Time

80 ml of 2.4×10^{-4} M $AuCl_4^-$ added back
to 100 ml base sol (2.4×10^{-4} M $AuCl_4^-$ + 1.6×10^{-3} M Citrate) at 65 °C

APPENDIX B

Reaction Series Two Data and Plots

Table 1

Reaction Series Two Base Sol Absorbance Data

Base Sol = 100 ml of 2.4×10^{-4} M $HAuCl_4$ + 1.6×10^{-3} M Citrate

λ (nm)	Absorbance at 0 hrs.
490	0.550
500	0.627
510	0.702
520	0.745
525	0.746
530	0.730
540	0.657
550	0.550
560	0.442
570	0.352
580	0.281
590	0.224
600	0.174
610	0.141

Table 2

Reaction 1 Absorbance Data

To 100 ml of initial sol (2.4×10^{-4} M $HAuCl_4$ + 1.6×10^{-3} M Citrate) add 1 ml of 2.4×10^{-4} M $HAuCl_4$ and 99 ml H_20.

λ (nm)	0.417 hr	2.08 hr	4.55 hr	30 hr	0 hr
490	0.223	0.243	0.259	0.227	0.550
500	0.262	0.284	0.302	0.267	0.627
510	0.303	0.327	0.346	0.307	0.702
520	0.333	0.357	0.377	0.332	0.745
525	0.340	0.364	0.383	0.334	0.746
530	0.340	0.362	0.380	0.329	0.730
540	0.321	0.340	0.355	0.297	0.657
550	0.284	0.298	0.310	0.249	0.550
560	0.245	0.256	0.266	0.204	0.442
570	0.208	0.218	0.228	0.168	0.352
580	0.178	0.188	0.199	0.142	0.281
590	0.148	0.159	0.170	0.121	0.224
600	0.118	0.128	0.141	0.097	0.174
610	0.098	0.111	0.123	0.079	0.141

Table 3

Reaction 2 Absorbance Data

To 100 ml of initial sol (2.4×10^{-4} M $HAuCl_4$ + 1.6×10^{-3} M Citrate) add 20 ml of 2.4×10^{-4} M $HAuCl_4$ and 80 ml H_20.

λ (nm)	0.112 hr	2 hr	4.45 hr	30 hr	0 hr
490	0.216	0.246	0.287	0.293	0.550
500	0.252	0.284	0.330	0.342	0.627
510	0.292	0.326	0.377	0.391	0.702
520	0.326	0.363	0.416	0.421	0.745
525	0.337	0.375	0.429	0.423	0.746
530	0.342	0.383	0.434	0.414	0.730
540	0.337	0.381	0.425	0.370	0.657
550	0.314	0.361	0.394	0.306	0.550
560	0.285	0.333	0.355	0.247	0.442
570	0.253	0.302	0.315	0.202	0.352
580	0.223	0.270	0.278	0.171	0.281
590	0.191	0.235	0.241	0.146	0.224
600	0.157	0.197	0.203	0.118	0.174
610	0.133	0.170	0.177	0.099	0.141

Table 4

Reaction 3 Absorbance Data

To 100 ml of initial sol (2.4×10^{-4} M $HAuCl_4$ + 1.6×10^{-3} M Citrate) add 40 ml of 2.4×10^{-4} M $HAuCl_4$ and 60 ml H_2O.

λ (nm)	0.25 hr	1.85 hr	4.3 hr	30 hr	0 hr
490	0.220	0.244	0.268	0.369	0.550
500	0.256	0.281	0.307	0.429	0.627
510	0.296	0.324	0.351	0.491	0.702
520	0.331	0.361	0.391	0.529	0.745
525	0.343	0.374	0.405	0.531	0.746
530	0.350	0.383	0.414	0.521	0.730
540	0.348	0.384	0.415	0.465	0.657
550	0.329	0.367	0.397	0.383	0.550
560	0.303	0.342	0.371	0.304	0.442
570	0.272	0.312	0.340	0.244	0.352
580	0.242	0.280	0.308	0.200	0.281
590	0.209	0.245	0.272	0.166	0.224
600	0.172	0.207	0.232	0.133	0.174
610	0.148	0.180	0.203	0.108	0.141

Table 5

Reaction 4 Absorbance Data

To 100 ml of initial sol (2.4 x 10^{-4} M $HAuCl_4$ + 1.6 x 10^{-3} M Citrate) add 70 ml of 2.4 x 10^{-4} M $HAuCl_4$ and 30 ml H_20.

λ (nm)	0.367 hr	1.68 hr	4.15 hr	30 hr	0 hr
490	0.222	0.251	0.273	0.433	0.550
500	0.258	0.289	0.312	0.499	0.627
510	0.298	0.332	0.357	0.572	0.702
520	0.333	0.371	0.398	0.627	0.745
525	0.346	0.385	0.413	0.639	0.746
530	0.353	0.394	0.423	0.640	0.730
540	0.353	0.397	0.427	0.604	0.657
550	0.336	0.382	0.412	0.531	0.550
560	0.311	0.358	0.388	0.446	0.442
570	0.281	0.329	0.359	0.369	0.352
580	0.252	0.298	0.328	0.306	0.281
590	0.220	0.262	0.291	0.254	0.224
600	0.184	0.223	0.251	0.206	0.174
610	0.158	0.195	0.222	0.169	0.141

Table 6

Reaction 5 Absorbance Data

To 100 ml of initial sol (2.4×10^{-4} M $HAuCl_4$ + 1.6×10^{-3} M Citrate) add 98 ml of 2.4×10^{-4} M $HAuCl_4$ and 2 ml H_2O.

λ (nm)	0.433 hr	1.6 hr	4.067 hr	30 hr	0.0 hr
490	0.259	0.285	0.312	0.509	0.550
500	0.296	0.324	0.353	0.584	0.627
510	0.339	0.369	0.400	0.666	0.702
520	0.377	0.411	0.444	0.728	0.745
525	0.391	0.427	0.461	0.742	0.746
530	0.400	0.437	0.473	0.742	0.730
535			0.480		
540	0.402	0.443	0.481	0.698	0.657
545			0.478		
550	0.386	0.430	0.469	0.612	0.550
560	0.362	0.407	0.447	0.514	0.442
570	0.333	0.378	0.418	0.427	0.352
580	0.302	0.346	0.386	0.356	0.281
590	0.268	0.310	0.349	0.299	0.224
600	0.230	0.269	0.306	0.245	0.174
610	0.202	0.240	0.274	0.210	0.141

Table 7

Reaction 6 Absorbance Data

To 100 ml of initial sol (2.4×10^{-4} M $HAuCl_4$ + 1.6×10^{-3} M Citrate) add 40 ml of 4.871×10^{-3} M $HAuCl_4$ and 60 ml H_20.

λ (nm)	0.3 hr	0.833 hr	3.23 hr	30 hr	0.0 hr
490	0.344	1.152	2.606	2.794	0.550
500	0.379	1.257	2.988	3.224	0.627
510	0.421	1.388	3.429	3.755	0.702
520	0.460	1.519	3.856	4.182	0.745
525	0.469	1.642	4.002	4.306	0.746
530	0.486	1.624	4.082	4.360	0.730
540	0.494	1.694	4.096	4.295	0.657
550	0.487	1.724	3.907	3.998	0.550
560	0.474	1.720	3.524	3.451	0.442
570	0.454	1.679	3.035	2.883	0.352
580	0.431	1.611	2.521	2.310	0.281
590	0.402	1.518	2.050	1.831	0.224
600	0.367	1.409	1.642	1.437	0.174
610	0.349	1.273	1.321	1.139	0.141

Table 8

Reaction 7 Absorbance Data

To 100 ml of initial sol (2.4 x 10^{-4} M $HAuCl_4$ + 1.6 x 10^{-3} M Citrate) add 100 ml of 4.871 x10^{-3} M $HAuCl_4$ and 0 ml H_2O.

λ (nm)	0.3 hr	0.9 hr	0.0 hr
490	0.672	2.043	0.550
500	0.752	2.274	0.627
510	0.849	2.566	0.702
520	0.934	2.832	0.745
525	1.031	2.891	0.746
530	0.977	2.944	0.730
540	0.970	2.864	0.657
550	0.923	2.638	0.550
560	0.863	2.368	0.442
570	0.797	2.121	0.352
580	0.734	1.919	0.281
590	0.670	1.764	0.224
600	0.602	1.649	0.174
610	0.497	1.597	0.141

Table 9

Reaction Series Two Size vs. Time Data

Time (hr)	Size (nm)							
Rxn.	Base	C1	C2	C3	C4	C5	C6	C7
0.117	42.65		88.82					
0.250	42.65			92.40				
0.300	42.65						33.8	39.5
0.300	42.65							
0.367	42.65				111.7			
0.417	42.65	44.0						
0.433	42.65					179.2		
0.833	42.65						32.5	
0.900	42.65							46.0
1.600	42.65					140.1		
1.680	42.65				96.3			
1.850	42.65			79.32				
1.980	42.65		84.68					
2.083	42.65	48.2						
3.230	42.65						32.2	
3.530	42.65							62.2
4.067	42.65					125.3		
4.150	42.65				95.3			
4.300	42.65			83.28				
4.450	42.65		73.97					
4.550	42.65	68.8						

Figure 1

Reaction 1 Absorbance over Time

To 100 ml of initial sol (2.4 x 10^{-4} M $HAuCl_4$ + 1.6 x 10^{-3} M Citrate) add 1 ml of 2.4 x 10^{-4} M $HAuCl_4$ and 99 ml H_2O.

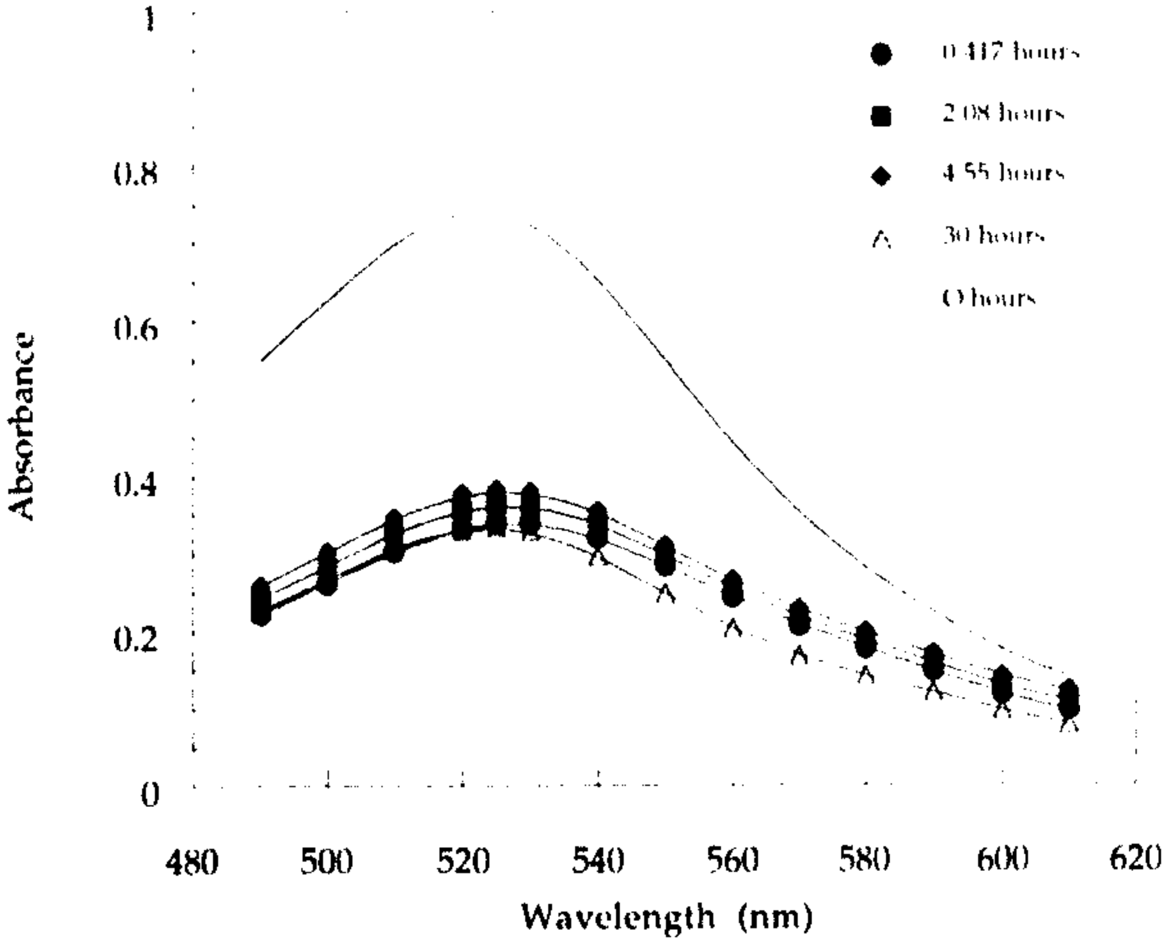
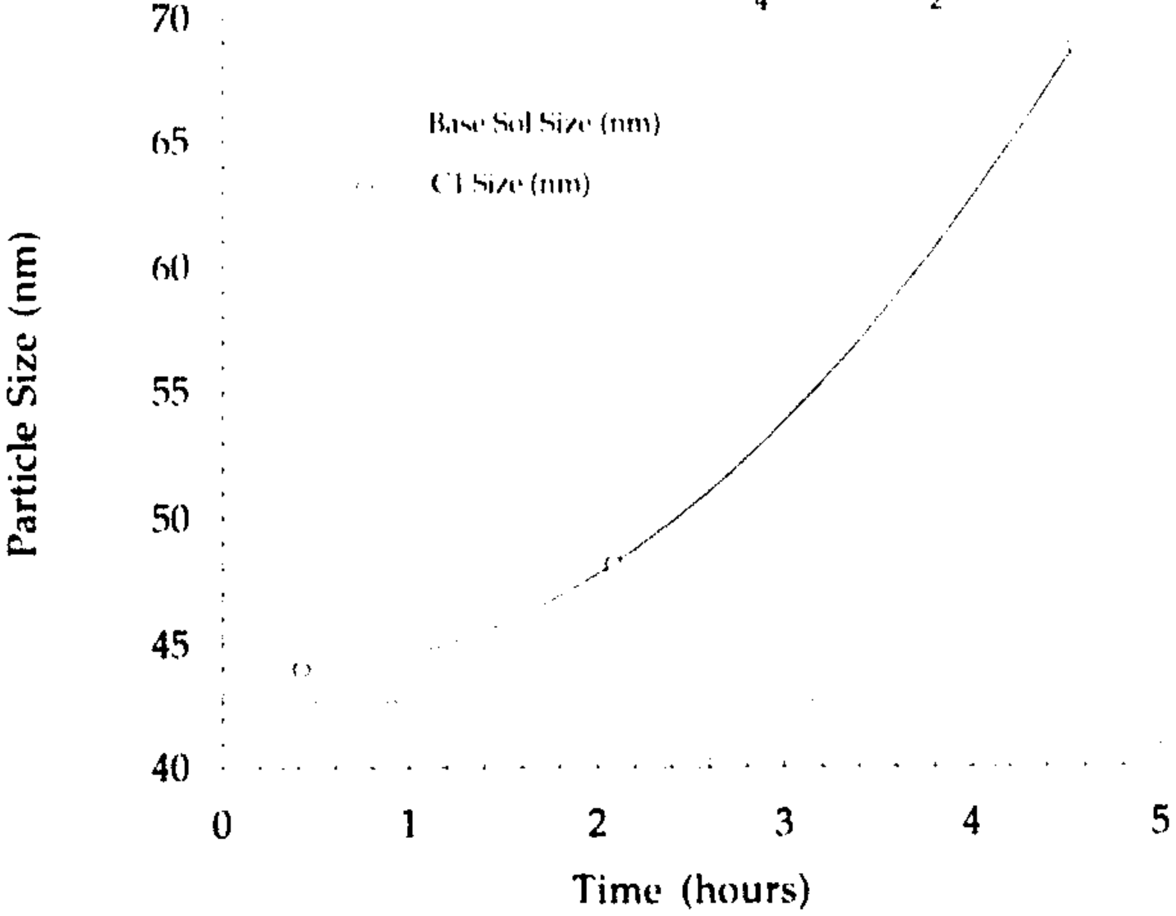


Figure 2

Reaction 1 Size vs. Time

To 100 ml of initial sol (2.4×10^{-4} M $HAuCl_4$ + 1.6×10^{-3} M Citrate) add 1 ml of 2.4×10^{-4} M $HAuCl_4$ and 99 ml H_2O



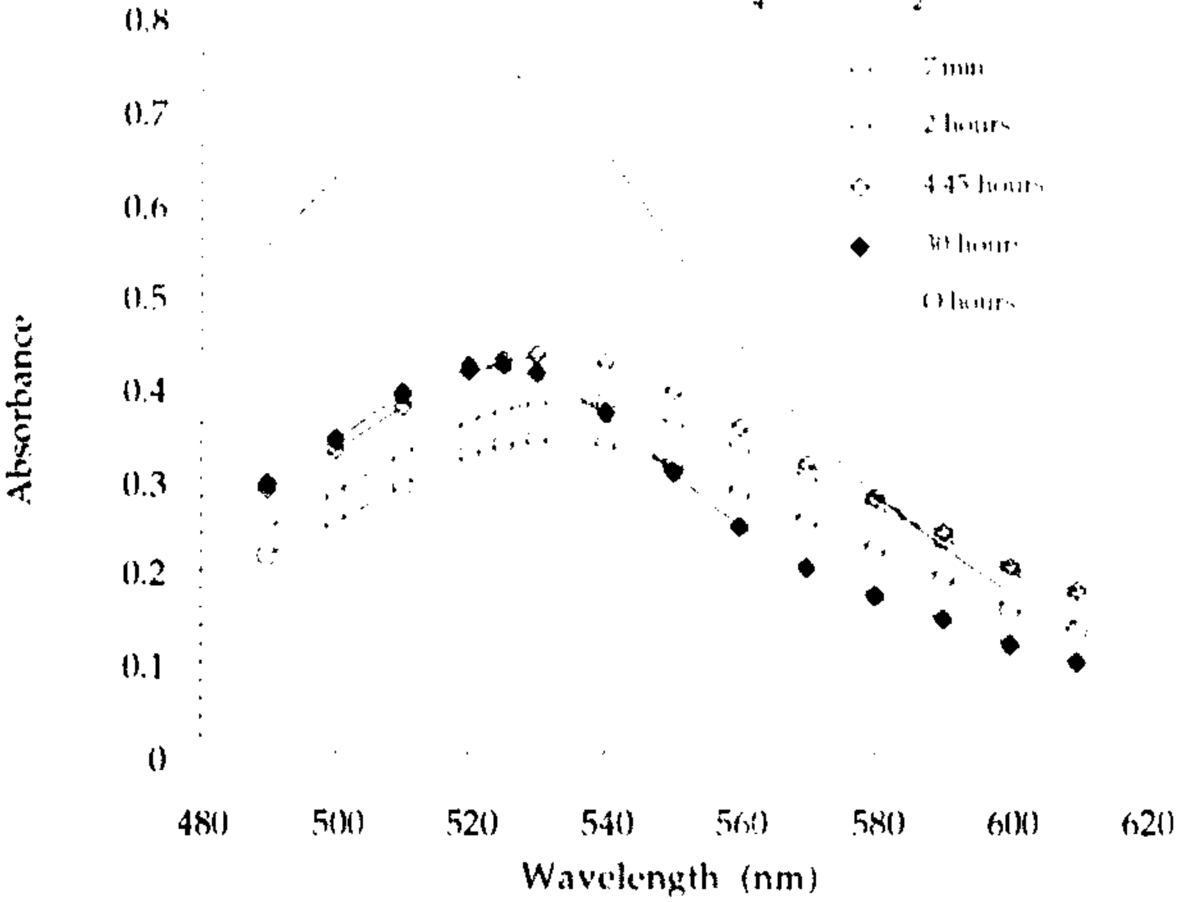


Figure 3
Reaction 2 Absorbance over Time

To 100 ml of initial sol (2.4×10^{-4} M $HAuCl_4$ + 1.6×10^{-3} M Citrate) add 20 ml of 2.4×10^{-4} M $HAuCl_4$ and 80 ml H_2O

Figure 4
Reaction 2 Size vs. Time

To 100 ml of initial sol (2.4×10^{-4} M $HAuCl_4$ + 1.6×10^{-3} M Citrate) add 20 ml of 2.4×10^{-4} M $HAuCl_4$ and 80 ml H_2O.

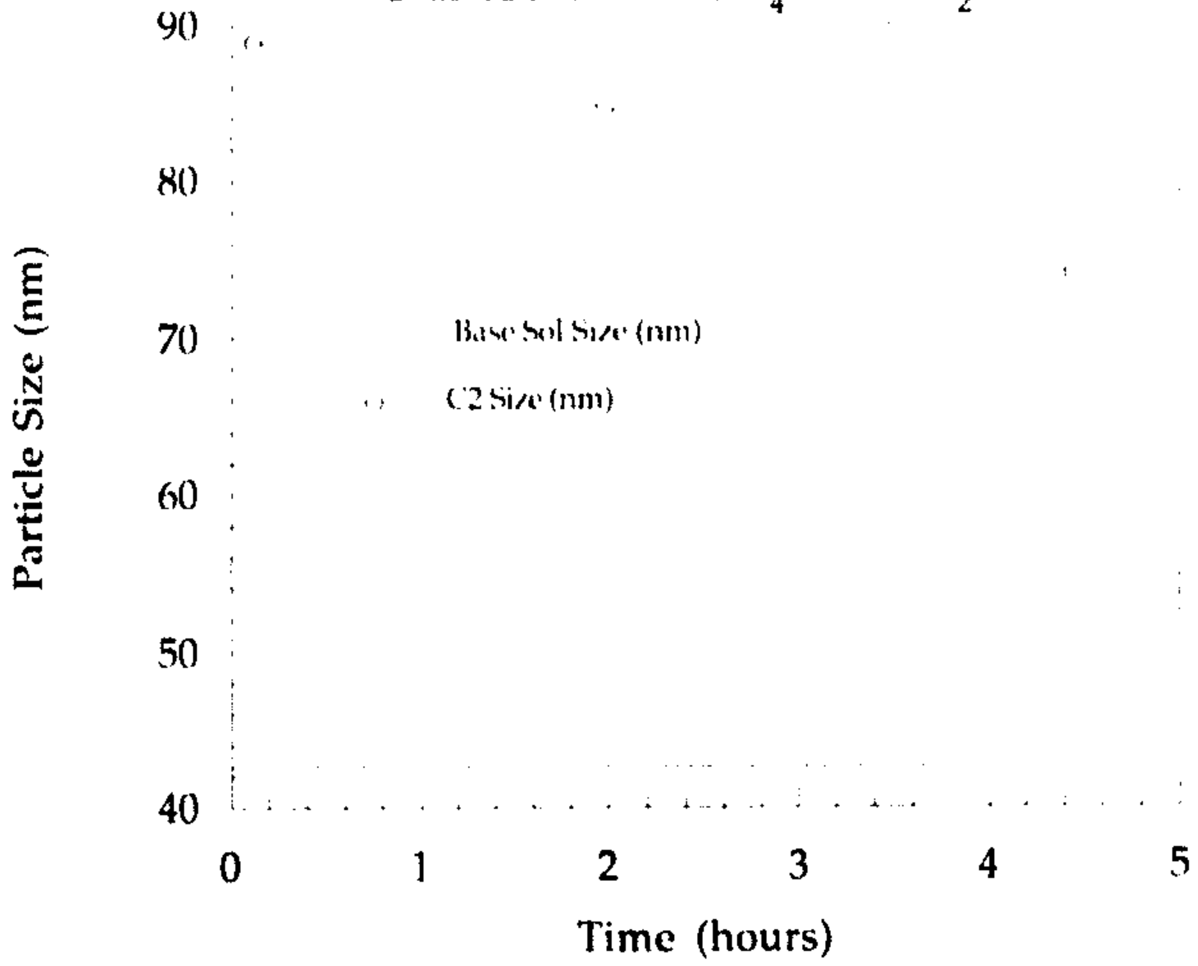


Figure 5
Reaction 3 Absorbance over Time

To 100 ml of initial sol (2.4 x 10^{-4} M $HAuCl_4$ + 1.6 x 10^{-3} M Citrate) add 40 ml of 2.4 x 10^{-4} M $HAuCl_4$ and 60 ml H_2O.

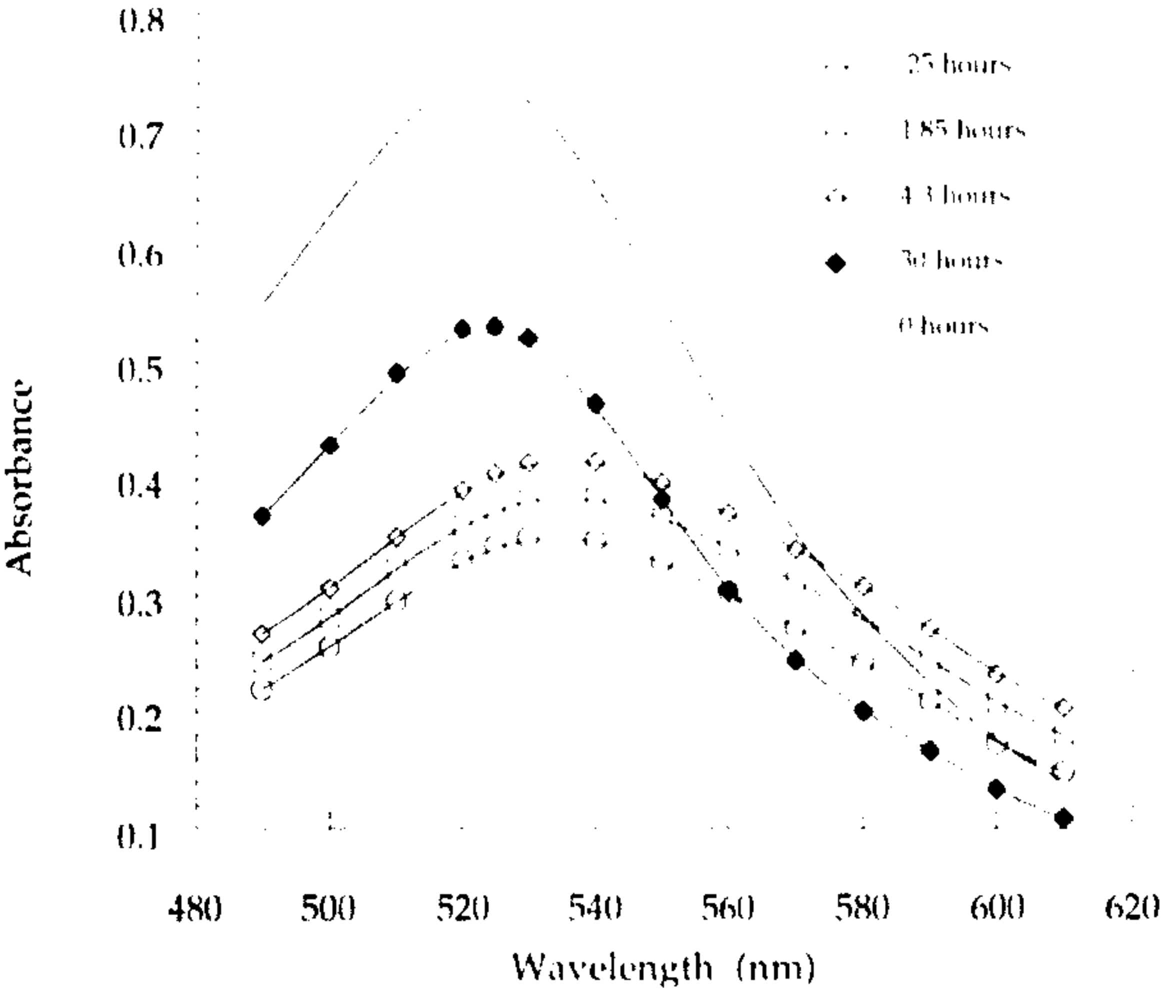


Figure 6
Reaction 3 Size vs. Time

To 100 ml of initial sol (2.4×10^{-4} M $HAuCl_4$ + 1.6×10^{-3} M Citrate) add 40 ml of 2.4×10^{-4} M $HAuCl_4$ and 60 ml H_2O.

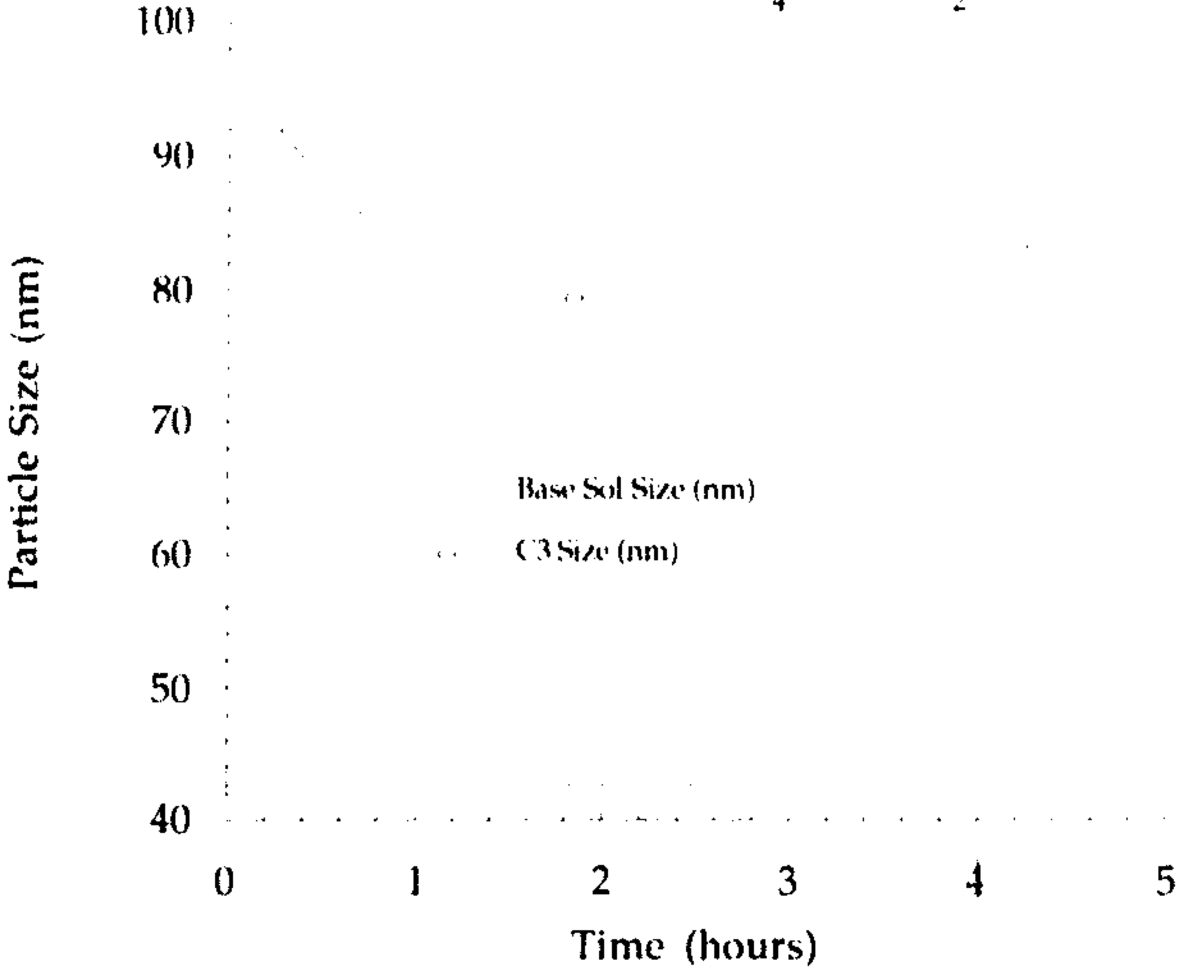


Figure 7
Reaction 4 Absorbance over Time

To 100 ml of initial sol (2.4 x 10^{-4} M $HAuCl_4$ + 1.6 x 10^{-3} M Citrate) add 70 ml of 2.4 x 10^{-4} M $HAuCl_4$ and 30 ml H_2O

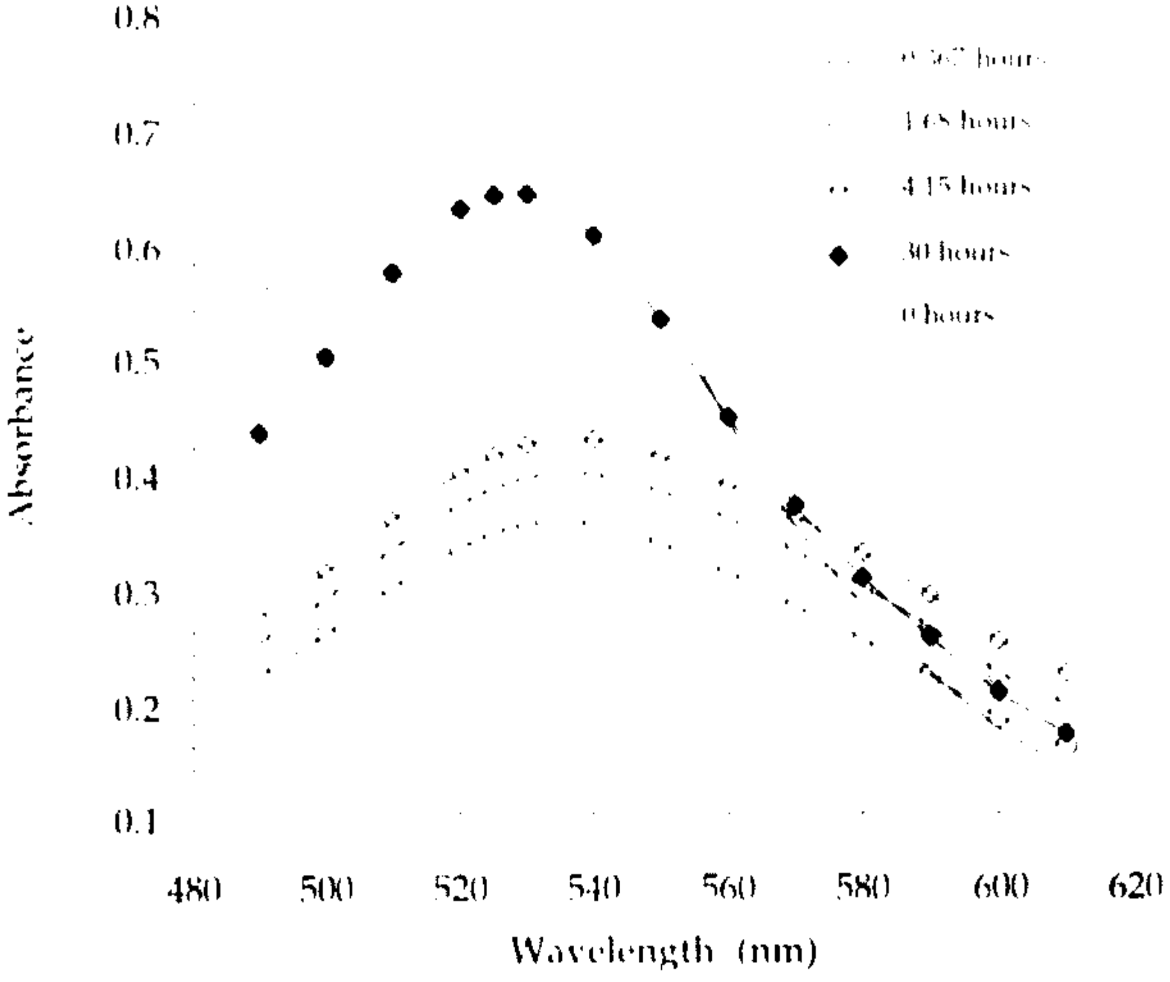


Figure 8
Reaction 4 Size vs. Time

To 100 ml of initial sol (2.4×10^{-4} M $HAuCl_4$ + 1.6×10^{-3} M Citrate) add 70 ml of 2.4×10^{-4} M $HAuCl_4$ and 30 ml H_2O.

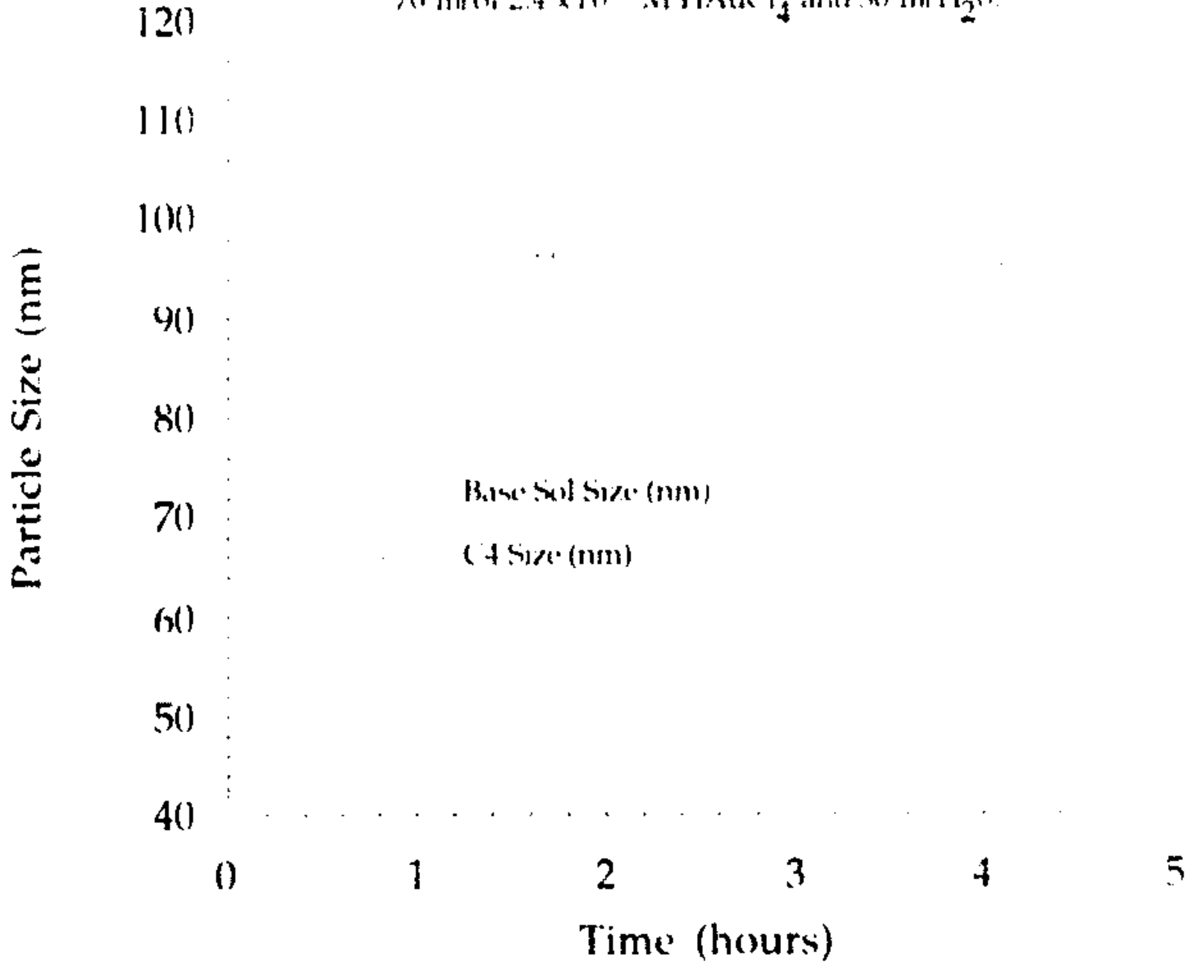


Figure 9
Reaction 5 Absorbance over Time

To 100 ml of initial sol (2.4×10^{-4} M $HAuCl_4$ + 1.6×10^{-3} M Citrate) add 98 ml of 2.4×10^{-4} M $HAuCl_4$ and 2 ml H_2O.

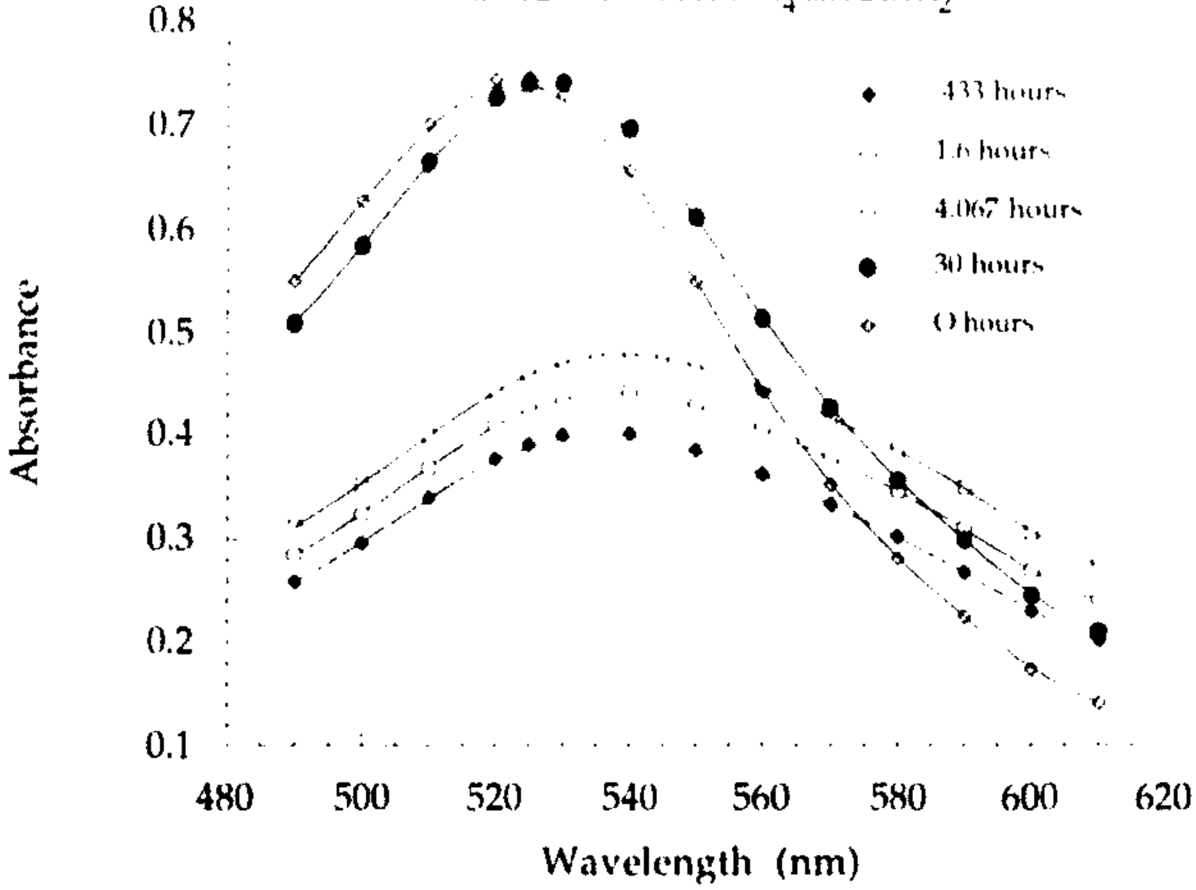


Figure 10
Reaction 5 Size vs. Time

To 100 ml of initial sol (2.4 x 10^{-4} M $HAuCl_4$ + 1.6 x 10^{-3} M Citrate) add 98 ml of 2.4 x 10^{-4} M $HAuCl_4$ and 2 ml H_2O.

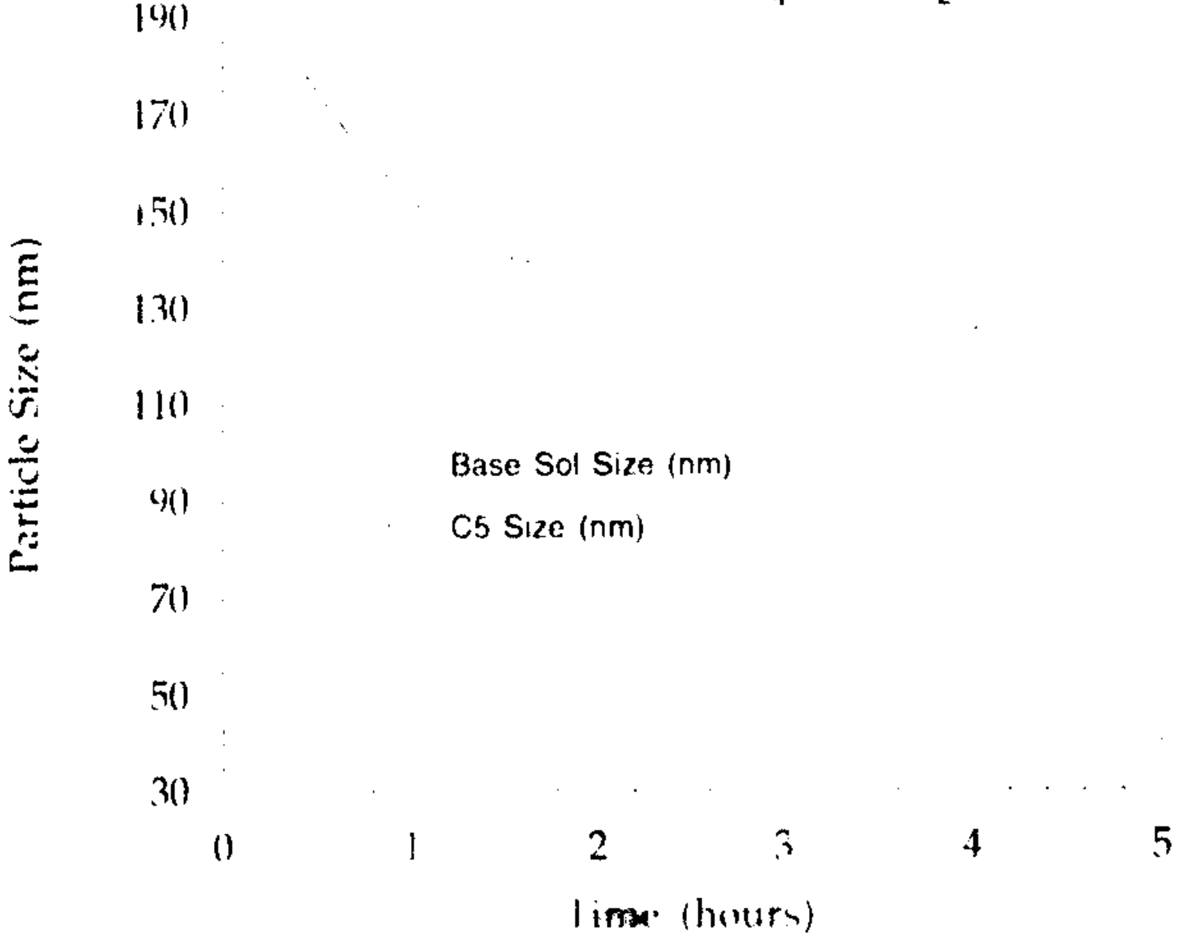
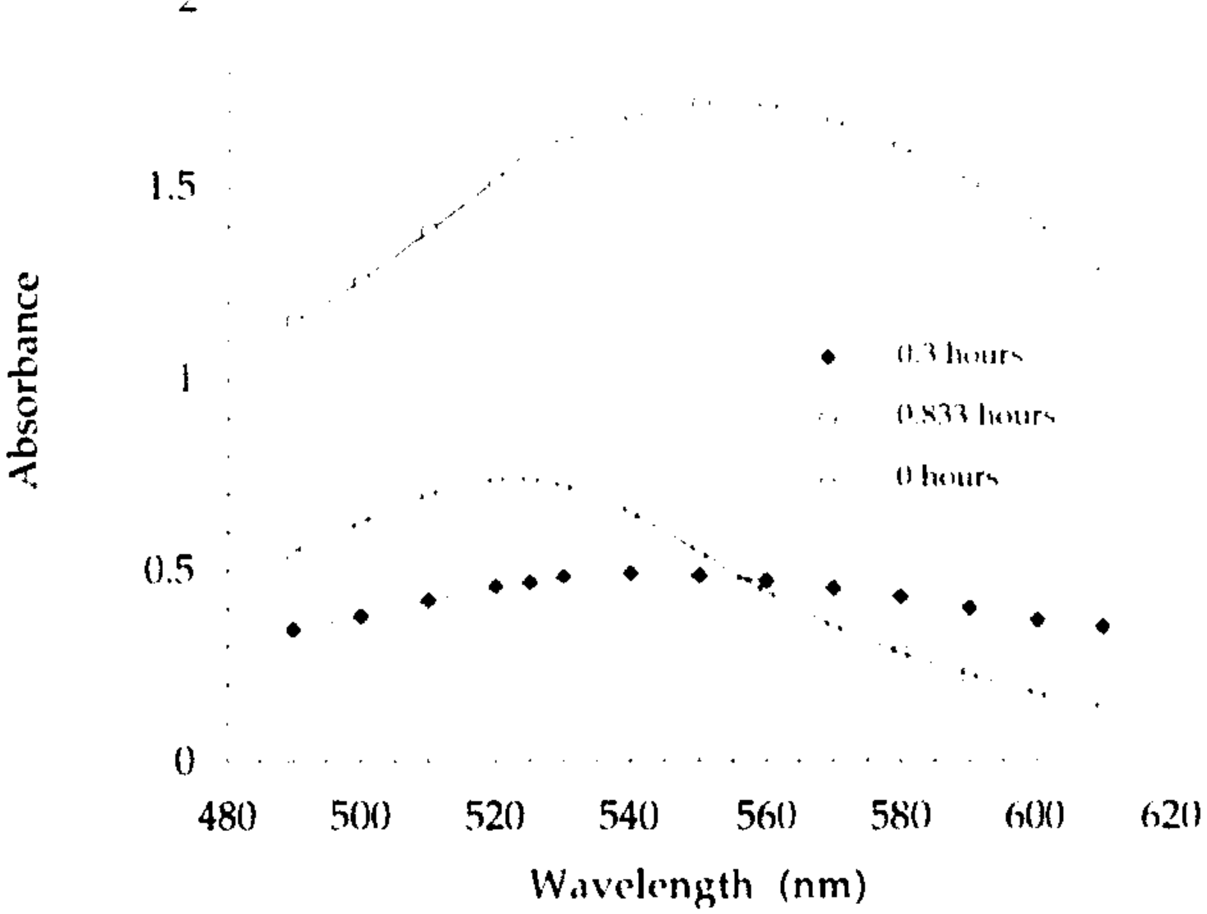


Figure 11
Reaction 6 Absorbance over Time

To 100 ml of initial sol (2.4×10^{-4} M $HAuCl_4$ + 1.6×10^{-3} M Citrate) add 40 ml of 4.871×10^{-3} M $HAuCl_4$ and 60 ml H_2O.



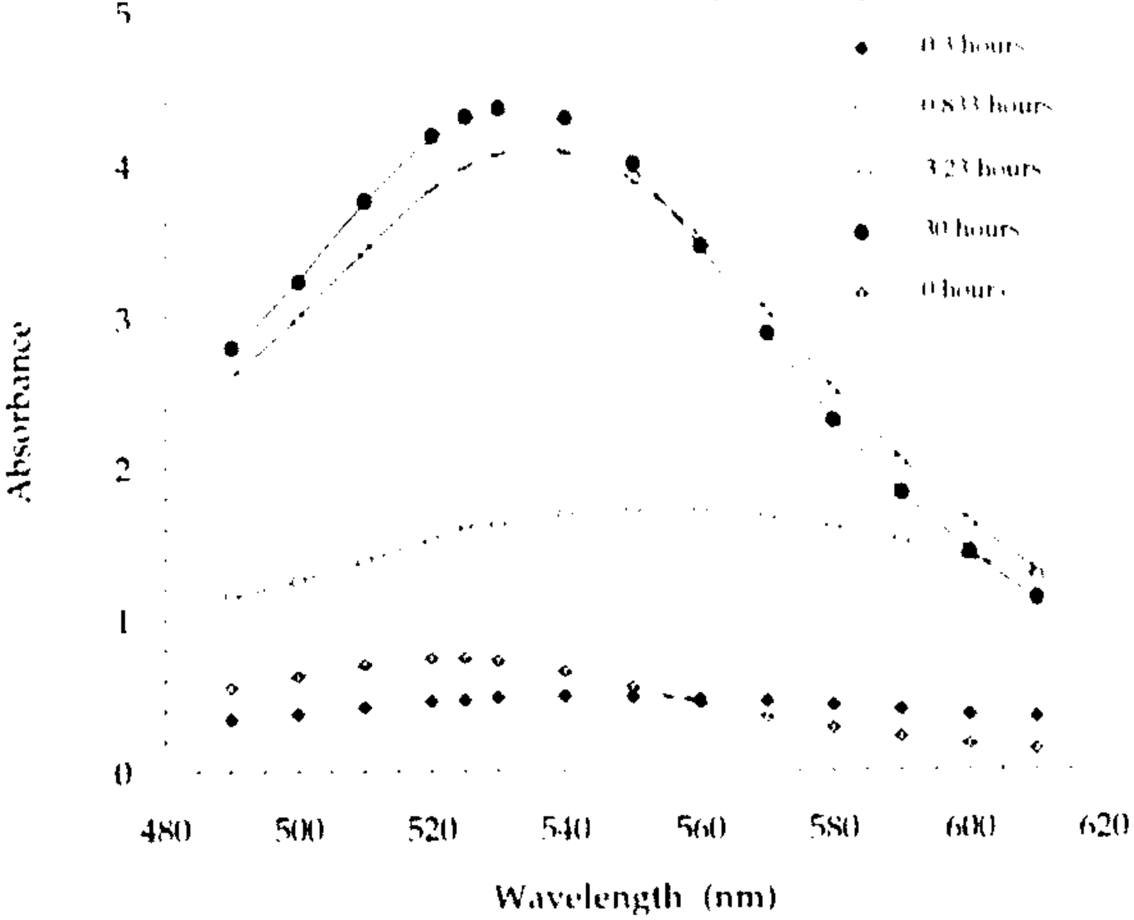


Figure 12
Reaction 6 Absorbance over Time, Graph 2

To 100 ml of initial sol (2.4 x 10^{-4} M $HAuCl_4$ + 1.6 x 10^{-3} M Citrate) add 40 ml of 4.871 x 10^{-3} M $HAuCl_4$ and 60 ml H_2O

Figure 13
Reaction 6 Size vs. Time

To 100 ml of initial sol (2.4 x 10^{-4} M $HAuCl_4$ + 1.6 x 10^{-3} M Citrate) add 40 ml of 4.871 x 10^{-3} M $HAuCl_4$ and 60 ml H_2O

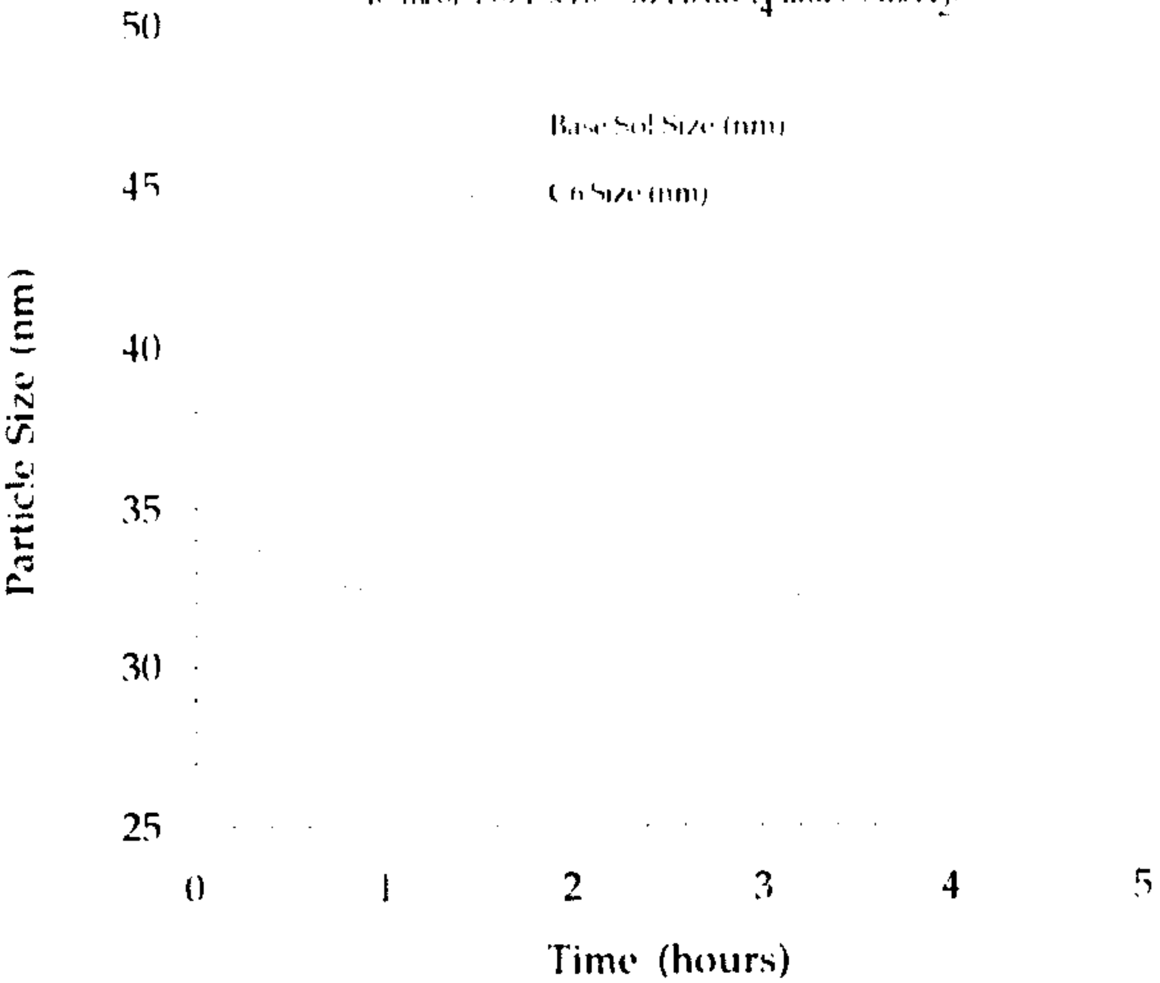


Figure 14
Reaction 7 Absorbance over Time

To 100 ml of initial sol (2.4 x 10^{-4} M $HAuCl_4$ + 1.6 x 10^{-3} M Citrate) add 100 ml of 4.871 x 10^{-3} M $HAuCl_4$ and 0 ml H_2O.

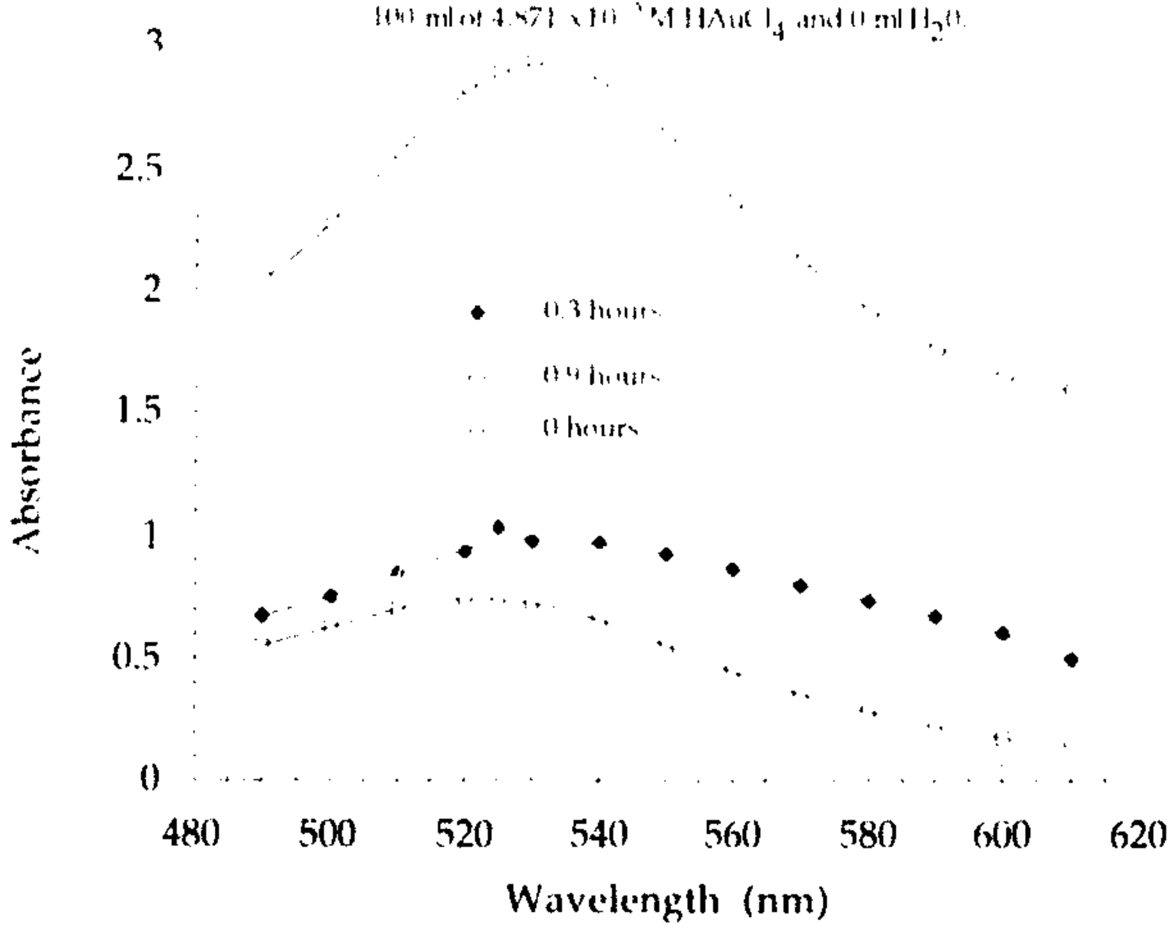
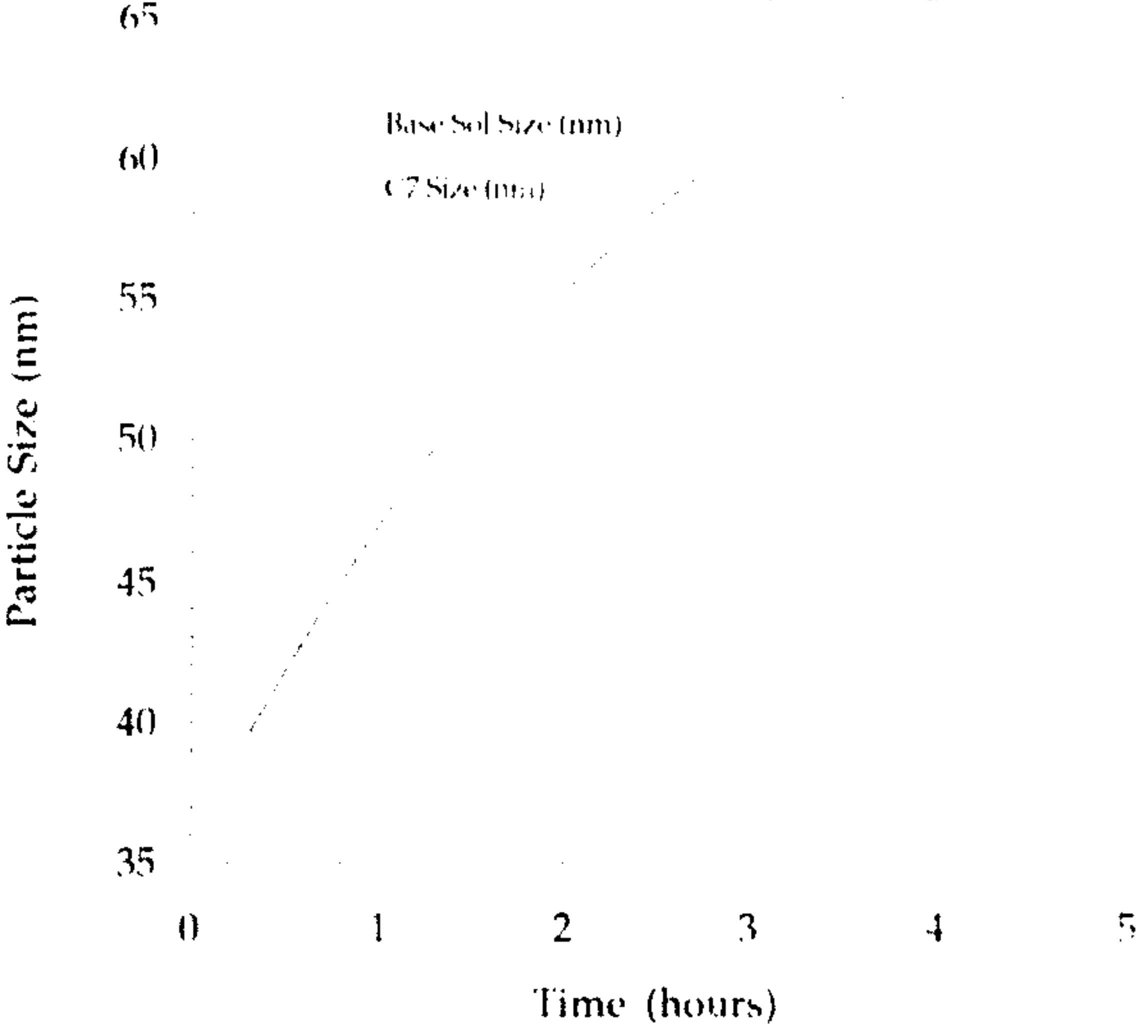


Figure 15
Reaction 7 Size vs. Time

To 100 ml of initial sol (2.4 x 10^{-4} M $HAuCl_4$ + 1.6 x 10^{-3} M Citrate) add 100 ml of 4.871 x 10^{-3} M $HAuCl_4$ and 0 ml H_2O



APPENDIX C

Reaction Series Three Data and Plots

Table 1

Reaction 1 Absorbance Data

Base Sol (1.2×10^{-5} M $HAuCl_4$ + 1.6×10^{-3} M Citrate) brought to 2.4×10^{-4} M $HAuCl_4$ and 1.6×10^{-3} M Citrate at 70 °C.

	Time (hours)									
λ (nm)	0	.0.1	0.67	0.88	1.05	1.2	1.75	2.28	2.8	5.97
490	0.000	0.000	0.070	0.347	0.527	0.534	0.538	0.530	0.487	0.542
500	0.000	0.000	0.089	0.406	0.619	0.628	0.630	0.622	0.572	0.636
510	0.000	0.000	0.112	0.473	0.734	0.736	0.738	0.729	0.672	0.743
520	0.000	0.000	0.134	0.523	0.795	0.805	0.809	0.804	0.740	0.814
530	0.000	0.000	0.151	0.532	0.794	0.799	0.802	0.803	0.737	0.801
540	0.000	0.000	0.162	0.494	0.715	0.712	0.714	0.723	0.657	0.705
550	0.000	0.002	0.167	0.409	0.588	0.584	0.586	0.592	0.544	0.569
560	0.000	0.022	0.174	0.358	0.465	0.460	0.468	0.469	0.436	0.447
570	0.000	0.039	0.176	0.305	0.366	0.369	0.378	0.377	0.355	0.356
580	0.013	0.056	0.175	0.262	0.303	0.303	0.316	0.311	0.299	0.292
590	0.023	0.066	0.168	0.228	0.253	0.255	0.270	0.261	0.255	0.244
600	0.027	0.069	0.156	0.198	0.212	0.215	0.232	0.220	0.219	0.203
610	0.023	0.065	0.139		0.178		0.199	0.184	0.184	0.16[illegible]
620	0.016	0.056	0.119							
630	0.007	0.044	0.097							
640	0.037	0.081	0.094							

time (hr)	λ_{max} (nm)
0.00	601.1
0.10	599.7
0.67	575.2
0.88	527.2
1.05	525.6
1.20	525.1
1.75	524.4
2.28	525.0
2.80	524.8
5.97	524.0

Table 2

Reaction 2 Absorbance Data

Base Sol (2.4×10^{-5} M $HAuCl_4$ + 1.6×10^{-3} M Citrate) brought to 2.4×10^{-4} M $HAuCl_4$ and 1.6×10^{-3} M Citrate at 70 °C.

	Time (hours)									
λ (nm)	0.0	0.08	.0.4	0.67	0.8	0.95	1.07	1.53	2.57	5.73
490	0.000	0.000	0.026	0.077	0.113	0.170	0.295	0.544	0.513	0.505
500	0.000	0.000	0.041	0.098	0.139	0.203	0.349	0.643	0.606	0.602
510	0.000	0.000	0.061	0.125	0.171	0.244	0.414	0.766	0.719	0.722
520	0.001	0.000	0.082	0.151	0.202	0.282	0.467	0.854	0.802	0.807
530	0.013	0.014	0.101	0.172	0.225	0.306	0.489	0.855	0.805	0.809
540	0.015	0.027	0.116	0.186	0.236	0.314	0.471	0.762	0.725	0.720
550	0.016	0.037	0.128	0.193	0.239	0.307	0.425	0.610	0.602	0.582
560	0.016	0.054	0.143	0.199	0.237	0.293	0.372	0.491	0.485	0.451
570	0.027	0.065	0.154	0.204	0.235	0.278	0.328	0.386	0.399	0.355
580	0.035	0.076	0.162	0.203	0.227	0.259	0.291	0.316	0.337	0.288
590	0.039	0.081	0.163	0.196	0.215	0.236	0.259	0.261	0.296	0.236
600	0.039	0.080	0.156	0.183	0.197	0.214	0.230	0.217	0.261	0.196
610	0.031	0.073	0.143	0.164	0.175	0.187	0.200	0.178	0.231	0.162
620	0.023	0.061	0.126	0.141	0.151					
630	0.015	0.046	0.106	0.118						
640	0.000	0.037	0.088							

time (hr.)	λ_{max}(nm)
0.00	594.0
0.08	594.7
0.40	585.4
0.67	574.0
0.80	561.0
0.95	539.1
1.07	530.8
1.53	525.4
2.57	525.7
5.73	525.5

Table 3

Reaction 3 Absorbance Data

Base Sol (6.0×10^{-5} M $HAuCl_4$ + 1.6×10^{-3} M Citrate) brought to 2.4×10^{-4} M $HAuCl_4$ and 1.6×10^{-3} M Citrate at 70 °C.

						Time (hours)							
λ (nm)		0	0.07	0.43	0.63	1.02	1.28	1.52	1.73	2.2	5.57	time (hr.)	λ_{max}(nm)
490	0.057	0.051	0.079	0.097	0.143	0.214	0.420	0.479	0.507	0.487		0.00	534.5
500	0.087	0.075	0.102	0.122	0.172	0.253	0.489	0.558	0.593	0.570		0.07	545.3
510	0.128	0.109	0.136	0.159	0.214	0.302	0.582	0.669	0.717	0.681		0.43	560.2
520	0.169	0.147	0.174	0.196	0.255	0.352	0.667	0.769	0.810	0.782		0.63	561.0
530	0.194	0.177	0.206	0.228	0.289	0.389	0.712	0.820	0.853	0.823		1.02	547.2
540	0.193	0.192	0.225	0.248	0.308	0.407	0.699	0.804	0.819	0.794		1.28	543.5
550	0.170	0.192	0.231	0.254	0.312	0.404	0.646	0.735	0.733	0.718		1.52	533.5
560	0.143	0.188	0.234	0.255	0.309	0.393	0.579	0.651	0.637	0.632		1.73	532.9
570	0.126	0.178	0.230	0.255	0.306	0.379	0.520	0.576	0.556	0.562		2.20	530.9
580	0.111	0.167	0.225	0.249	0.294	0.360	0.469	0.511	0.492	0.503		5.57	530.8
590	0.097	0.153	0.215	0.239	0.281	0.336	0.424	0.457	0.439	0.456			
600	0.084	0.137	0.200	0.220	0.261	0.312	0.383	0.405	0.390	0.411			
610	0.068	0.118	0.180	0.202	0.237	0.282	0.340	0.359	0.344	0.370			
620	0.051	0.097	0.158	0.178		0.251							
630		0.075	0.134	0.155									
640		0.055											

Table 4

Reaction Series Three Size vs. Time Data

	Reaction		
Time (min)	1	2	3
0	35.87	45.60	45.67
5	54.07	62.90	61.57
10	50.15	57.47	61.30
15	52.33	54.97	63.43
30	49.30	56.17	63.83
60	40.90	49.73	59.57
90	31.17	35.37	42.27
120	30.10	34.30	38.07

Figure 1
Reaction 1 Absorbance vs. Time

Base Sol (1.2e-5 M $HAuCl_4$ + 1.6e-3 M $Na_3C_6H_5O_7$) brought to 2.4e-4 M $HAuCl_4$ and 1.6e-3 M $Na_3C_6H_5O_7$

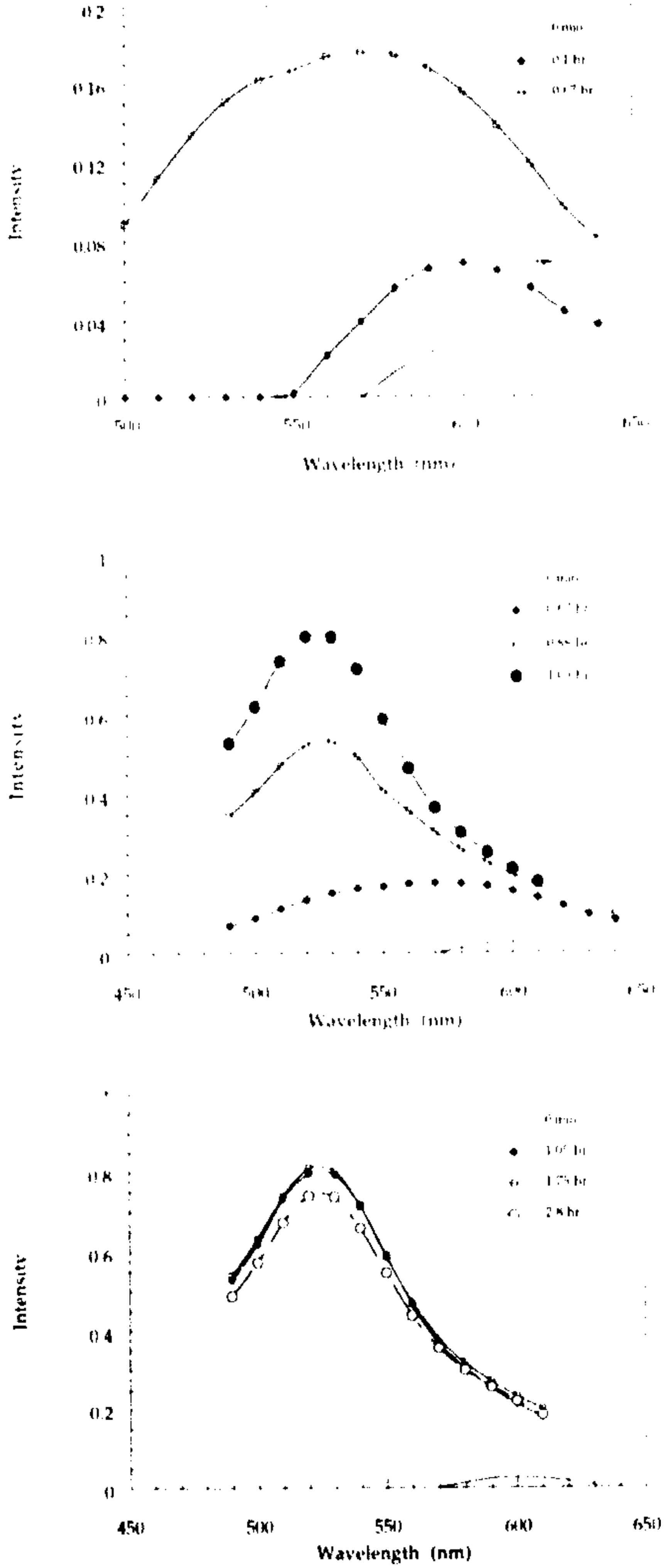


Figure 2
Reaction 1 Peak Absorbance vs. Time

Base Sol (1.2e-5 M HAucl$_4$ + 1.6e-3 M Na$_3$C$_6$H$_5$O$_7$) brought to 2.4e-4 M HAucl$_4$ and 1.6e-3 M Na$_3$C$_6$H$_5$O$_7$

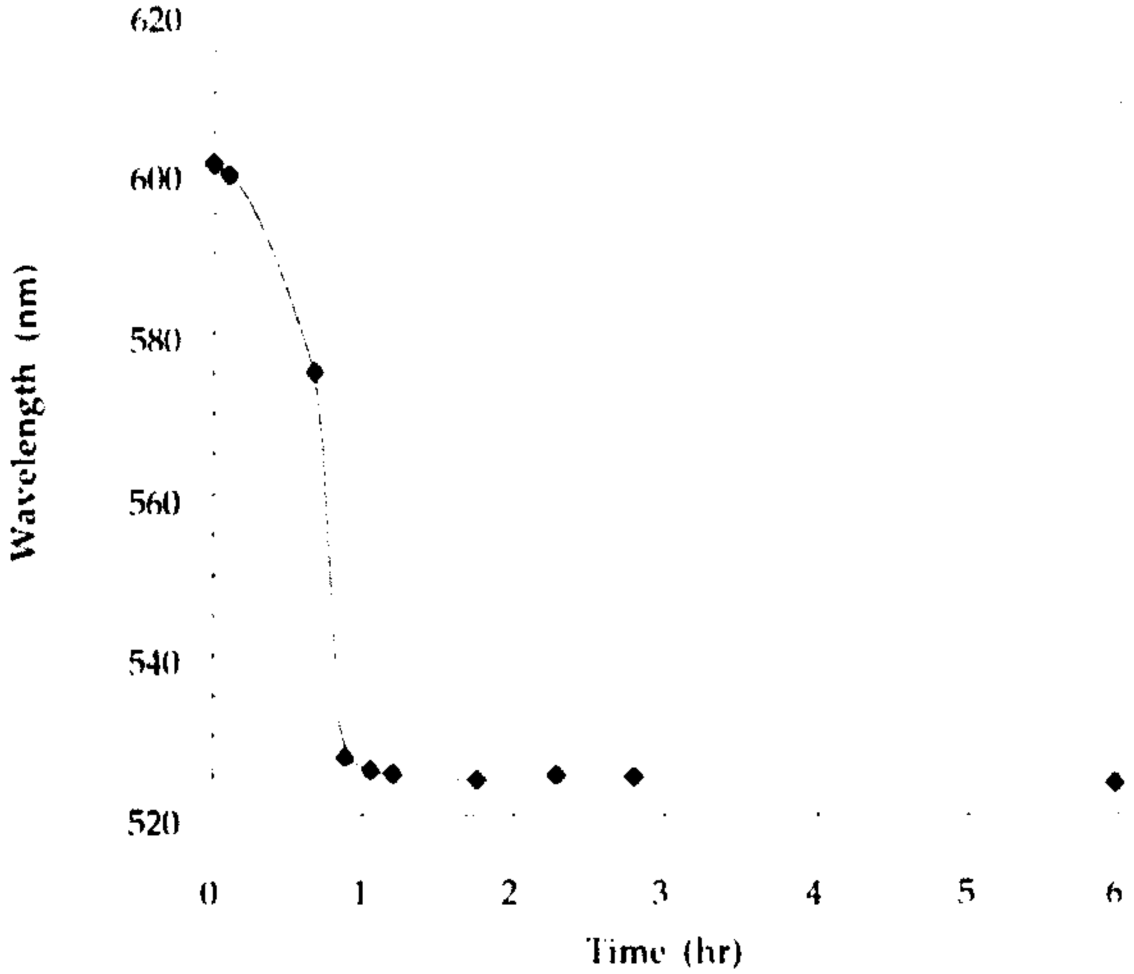


Figure 3
Reaction 1 Size vs. Time

Base sol (1.2×10^{-5} M $HAuCl_4$ + 1.6×10^{-3} M Citrate)
brought to 2.4 x 10-4 M $HAuCl_4$ and 1.6×10^{-3} M Citrate.

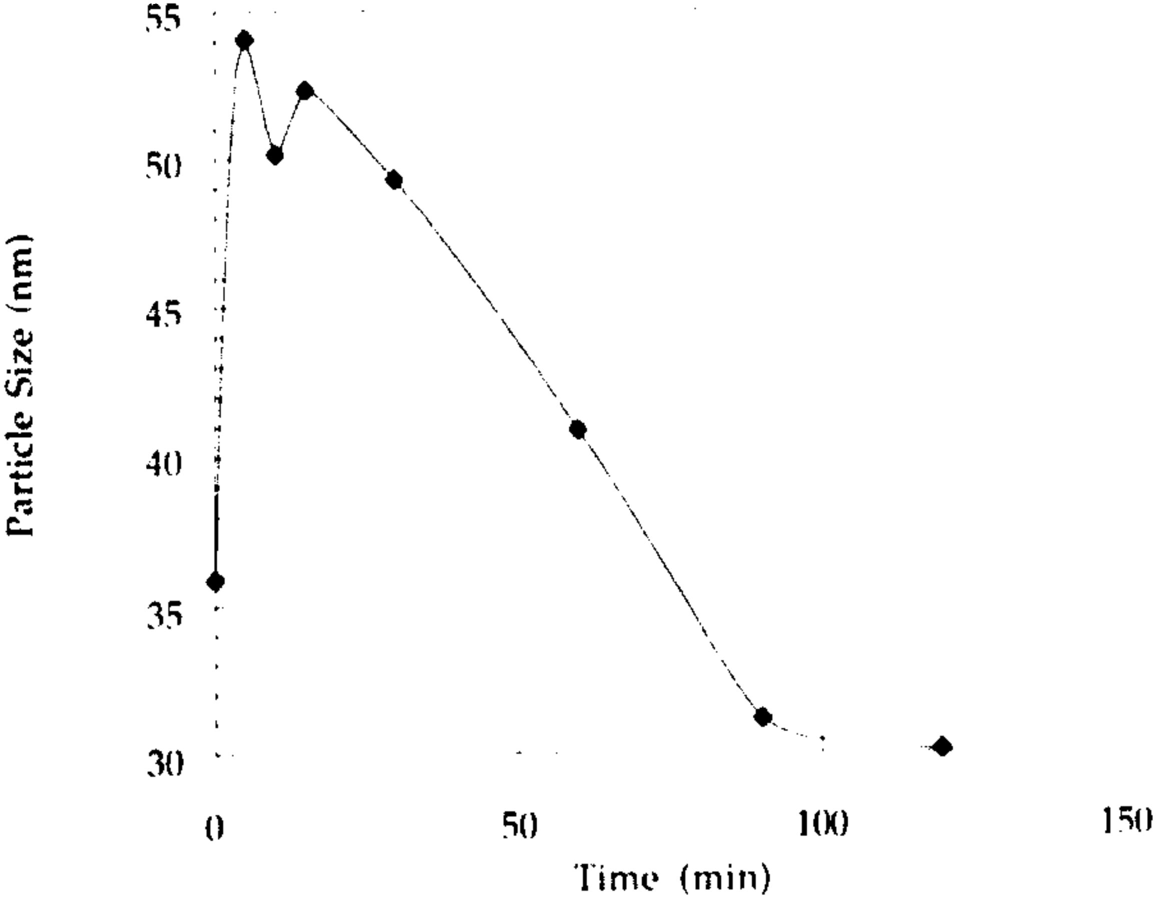


Figure 4
Reaction 2 Absorbance vs. Time

Base Sol (2.4e-5 M $HAucl_4$ + 1.6e-3 M $Na_3C_6H_5O_7$) brought
to 2.4e-4 M $HAucl_4$ and 1.6e-3 M $Na_3C_6H_5O_7$

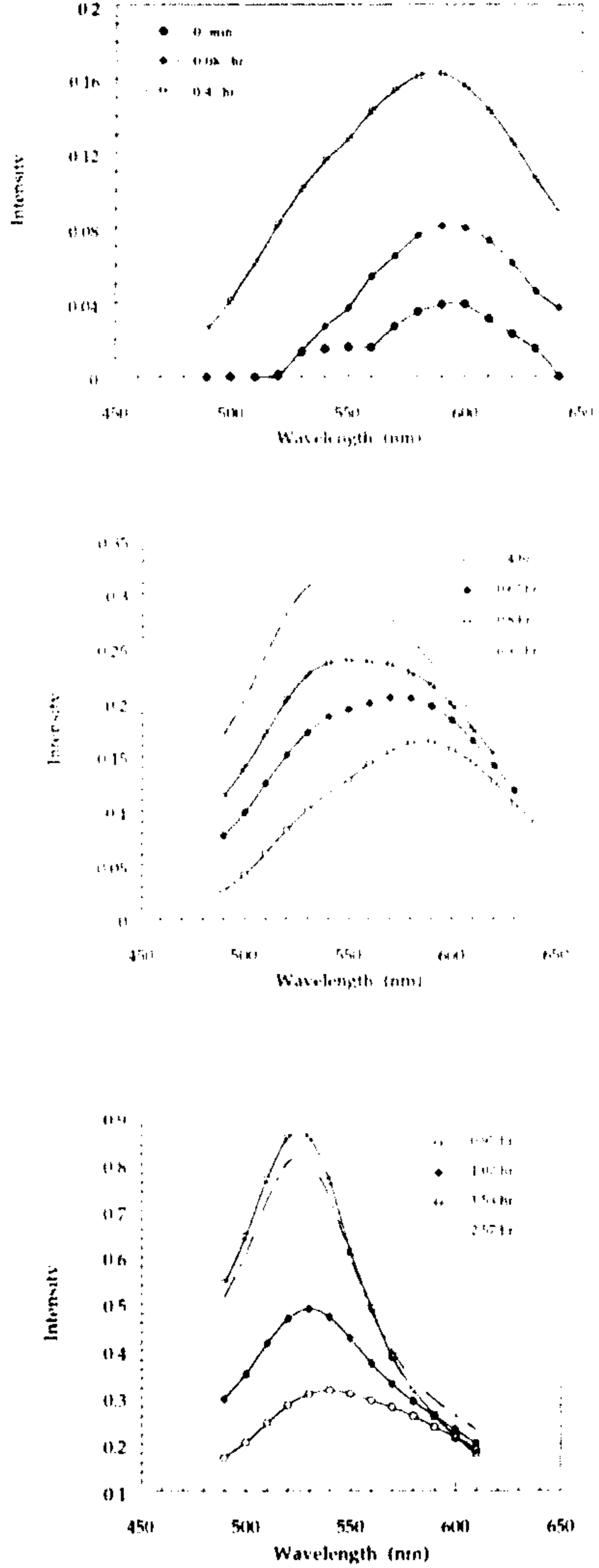


Figure 5
Reaction 2 Peak Absorbance vs. Time

Base Sol ($2.4e-5$ M $HAucl_4$ + $1.6e-3$ M $Na_3C_6H_5O_7$) brought to $2.4e-4$ M $HAucl_4$ and $1.6e-3$ M $Na_3C_6H_5O_7$.

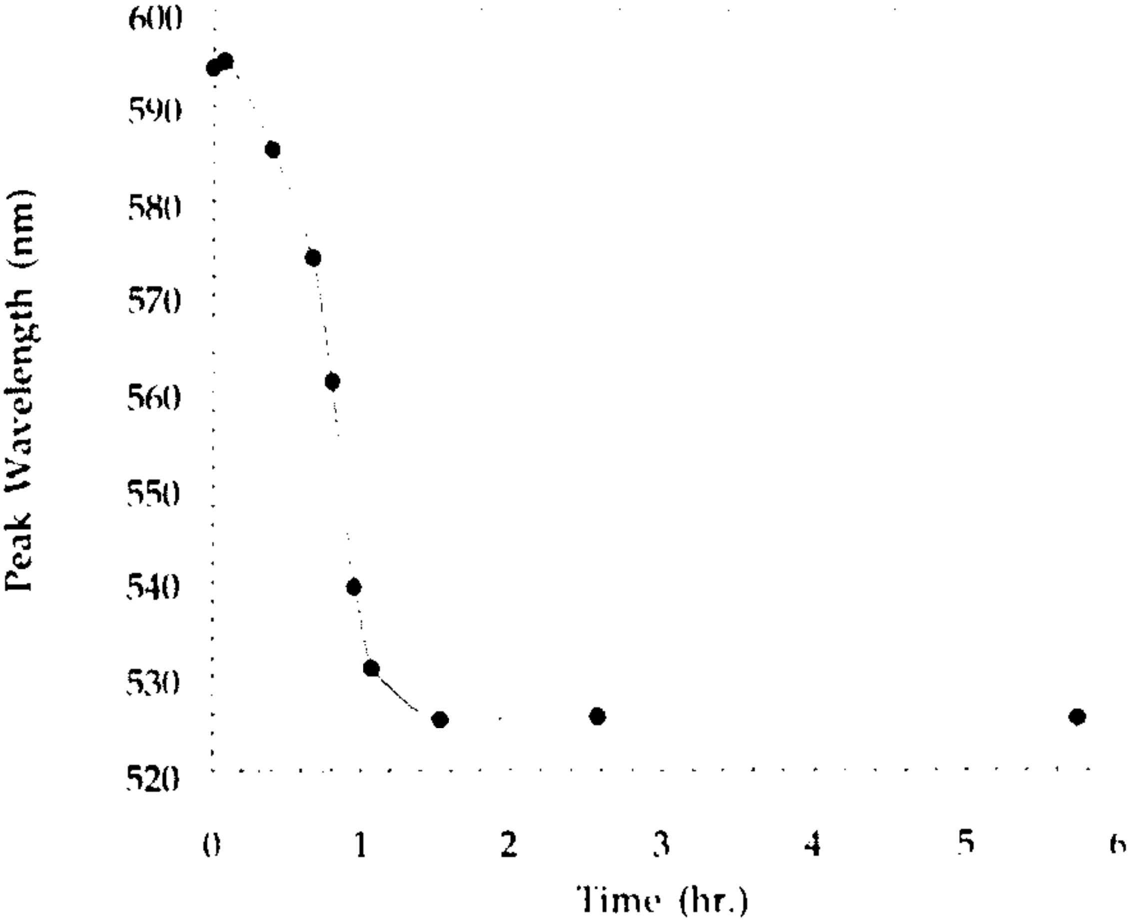


Figure 6

Reaction 2 Size vs. Time

Base sol (2.4×10^{-5} M $HAuCl_4$ + 1.6×10^{-3} M Citrate)

brought to 2.4 x 10-4 M $HAuCl_4$ and 1.6×10^{-3} M Citrate.

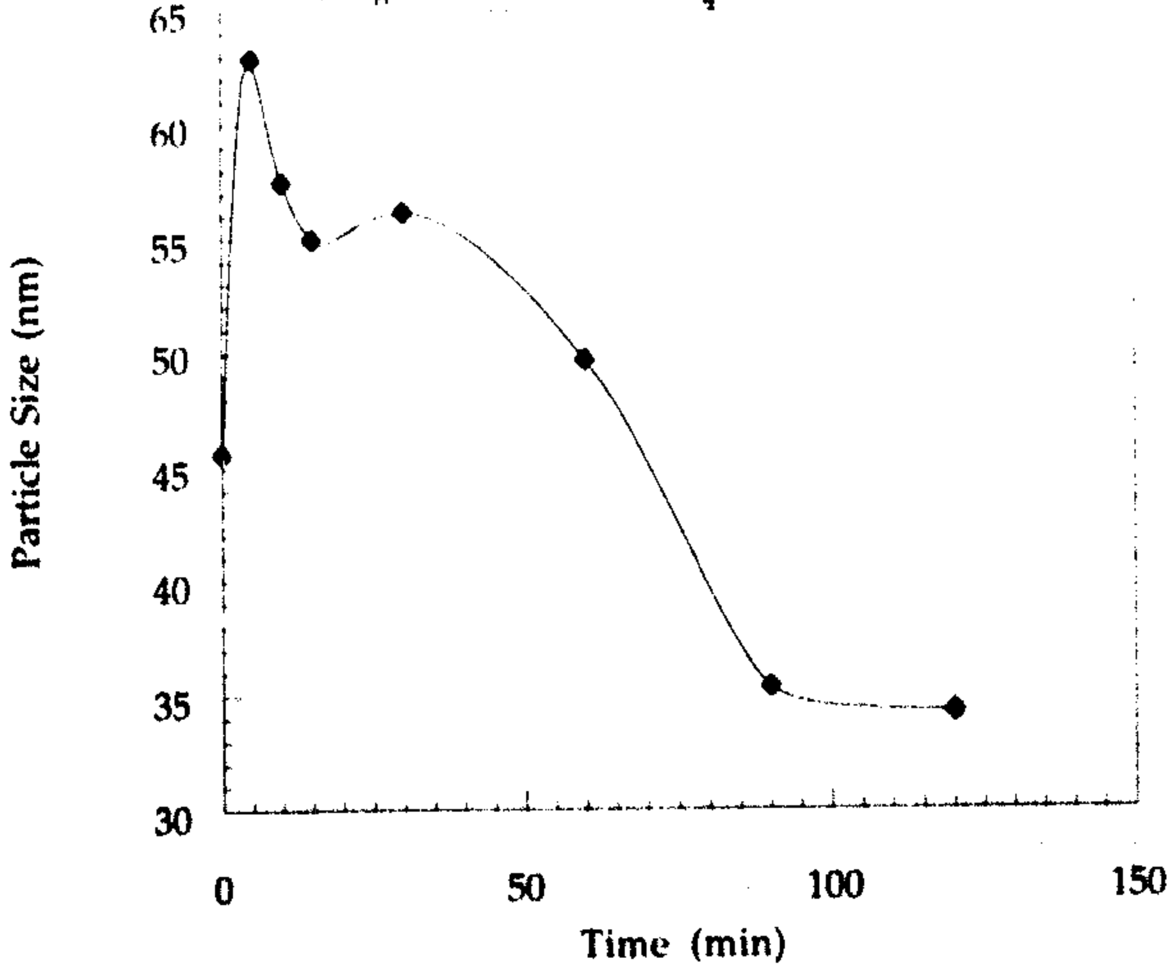


Figure 7
Reaction 3 Absorbance over Time

Base Sol (6.0e-5 M $HAuCl_4$ + 1.6e-3 M $Na_3C_6H_5O_7$) brought to 2.4e-4 M $HAuCl_4$ and 1.6e-3 M $Na_3C_6H_5O_7$

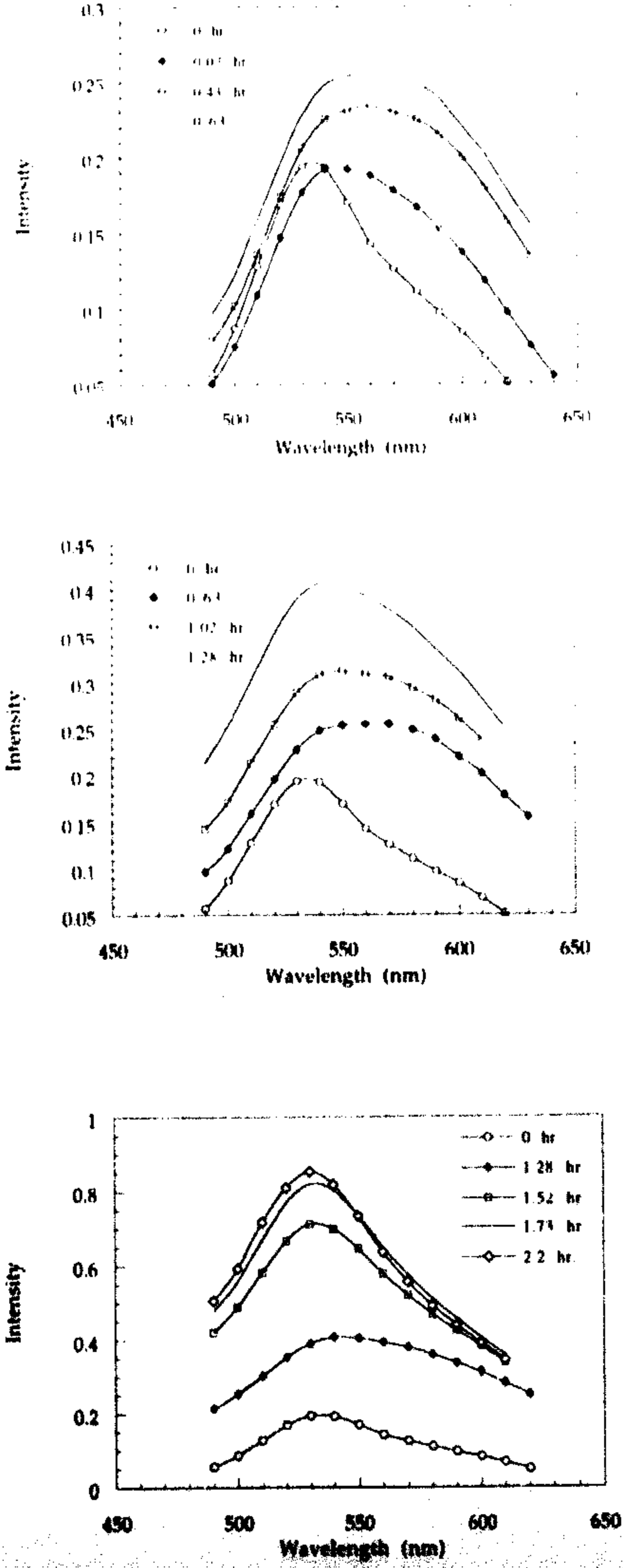


Figure 8
Reaction 3 Peak Absorbance vs. Time

Base Sol (6.0e-5 M $HAuCl_4$ + 1.0e-3 M $Na_3C_6H_5O_7$) brought to 2.4e-4 M $HAuCl_4$ and 1.0e-3 M $Na_3C_6H_5O_7$.

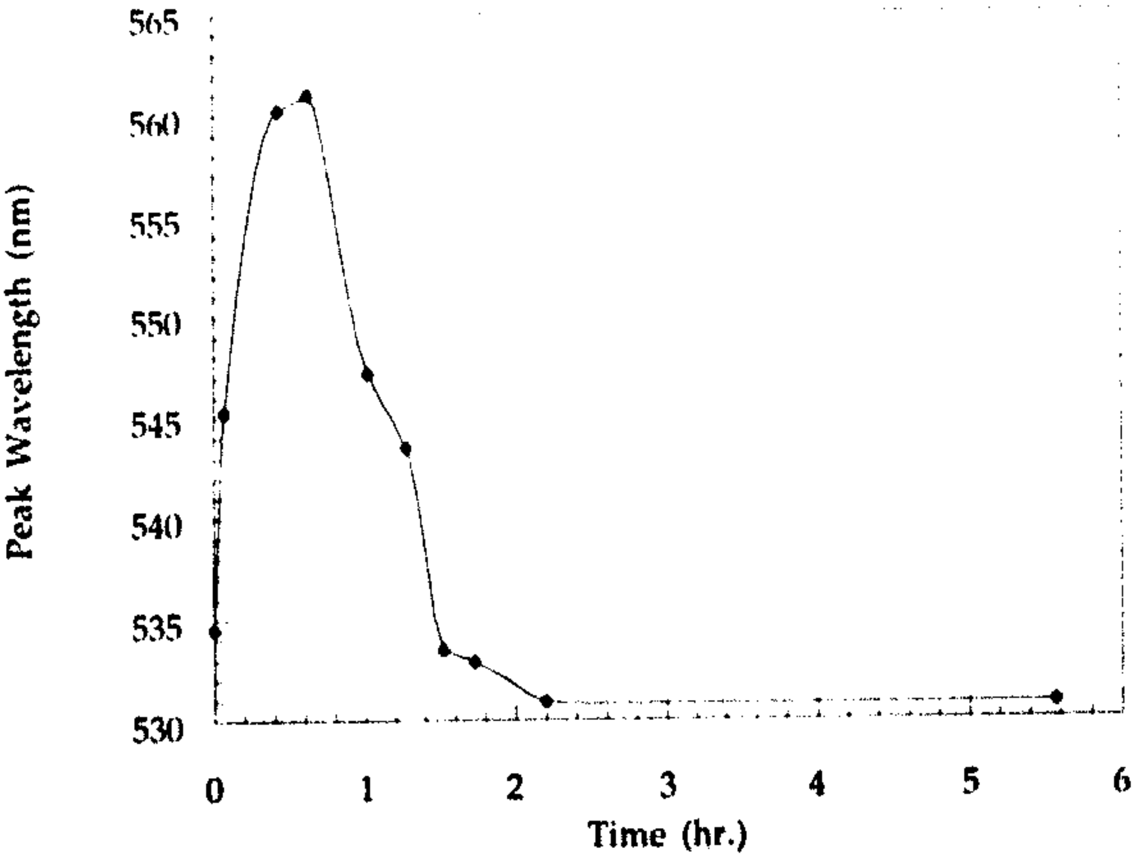


Figure 9
Reaction 3 Size vs. Time

Base sol (6.0×10^{-5} M $HAuCl_4$ + 1.6×10^{-3} M Citrate)
brought to 2.4 x 10-4 M $HAuCl_4$ and 1.6×10^{-3} M Citrate.