
Preparation and characterization of metal nanoparticles

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Abstract

Silver and gold nanoparticles are of great interest because of their unique properties, both catalytic and optical, which differ greatly from those of the bulk metals. The particles can be used to enhance imaging techniques in medical and research situations, improve the efficiency of reactions and reduce the amount of material needed in different products.

The properties of nanoparticles depend on their size and shape, and so it would be very useful to be able to control both of these properties in the fabrication process. An understanding of the stability of the particles and their sensitivity to light is also essential if they are to be used widely. Simple chemical procedures already exist to produce both silver and gold nanoparticles, using sodium citrate to reduce salts of the metals. Additionally, it has recently been proposed that silver nitrate can be reduced in a microwave oven without additional reducing agent. This is useful because the particles produced in this manner are purer and less contaminated than those produced via chemical reduction.

Therefore, in this paper we want to explore the parameters which govern the products formed from the reduction process with citrate as well as study the effect of microwaves on the reduction process. We will attempt to verify the possibility of producing silver nanoparticles without reducing agents. The stability of the nanoparticles produced will also be tested.

Our studies show that the ratio between sodium citrate and the metal ions is the crucial parameter in controlling the size of the nanoparticles produced via chemical reduction. By varying this, particles of sizes ranging from 8 to 50 nm have been produced. The nanoparticles produced in this manner are stable over time and retain their properties over the course of four months. We were not able to reproduce the results in which silver nanoparticles were produced in a microwave without additional reducing agent. Using the microwave oven as source of heat was a success, as this heating was faster and more localized than heating on a hot plate.

The nanoparticles produced were characterized in terms of their optical and structural properties, by analyzing the Brownian motion of the particles in solution and their extinction spectrum. The technique used to obtain the size of gold nanoparticles from their extinction spectrum proved very reliable and was in close agreement with the results obtained from the Brownian motion measurements.

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1 Introduction

Metal particles on the nanoscale are of great interest in a wide range of fields, including optics, catalysis and spectroscopy due to their properties, which are very different from those of the bulk metals[1]. The goal of this paper is to produce metal nanoparticles whose size can be controlled, and then to use state-of-the-art characterization methods to determine their physical properties.

Of particular interest are the interactions of nanoparticles particles with light, which are dominated by surface plasmon resonance (SPR). 'Plasmon' is the name given to the collective motion of electrons on the surface of particles caused by the interaction of the electrons with the electric component of light waves. At certain frequencies, a resonance effect is set up between the plasmons and the light wave, greatly increasing its intensity. This effect is potentially very useful for enhancing the Raman signal of molecules which is typically too weak to be detected easily. Raman scattering is the inelastic scattering of a photon striking a molecule. During this, the direction of propagation of the photon as well as the wavelength, changes. The exact spectrum of photons scattered after irradiation at different frequencies can be used to exactly identify substances[2]. Plasmon resonances can be used to increase the intensity of the Raman scattered so that it can easily be detected, even when coming from a single molecule.

Another interesting property of nanoparticles is their catalytic abilities. Nanoparticles are useful as catalysts because a very effective catalyst can be made using minimal amounts of material. It has previously been observed that the size, shape and aggregation state of the particles have a very great influence on their catalytic abilities [3]. A particle with many edge and corner atoms is more reactive than one with fewer [1]. Groups of small particles have been observed to be catalysts, even if the bulk material is non-reactive. One potential explanation for this lies in the electric properties of the nanoparticles[3]. Additionally, the surface area to volume ratio plays a large part in chemical reactivity, and the nanoparticles have a very large surface area compared to their volume[1]. This means that small catalytic properties might be enhanced.

As the properties of metallic nanoparticles depend to such a great extent on their size, shape and aggregation state[1], the ability to control these parameters is crucial. One of the most common preparation methods of nanoparticles, the reduction of a metal salt in aqueous solution, allows this to some extent. The salts of noble metals such as gold are in general unstable and hence are very easily reduced. This means that a wide variety of methods to carry out this process has already been discovered, and fine-grained control of the sizes of the nanoparticles has been available for many years [4]. However precise control of the shape of the resulting nanoparticles is still lacking[4].

In the case of silver nanoparticles, a small number of groups have reported success with the microwave-assisted reduction of silver nitrate [5][3]. It has been observed that under certain conditions, no extra reducing agent is required. This is potentially very useful, as it would lead the way to a cleaner, more efficient synthesis, where the difficulty of extracting the metal nanoparticles from the other chemicals in solution is greatly reduced. However, the chemical reduction of silver salts is still the most common production method [1].

Additional fabrication techniques exist and fall into two main categories: vapor condensation and solid-state processes. Vapor condensation techniques involve the evaporation of the solid metal followed by its condensation in a very controlled environment. The size and shape of the particles can be controlled through the specific parameters of the environment[6], such as temperature and concentrations of the different substances. Solid-state processes include simple grinding and milling techniques, which can also be used to create nanoparticles[6]. It is possible to create multi-metal nanoparticles by these techniques and tune them as wanted[7]. One other large part of the solid-state processes for producing nanoparticles is laser ablation. This is the process of hitting a solid plate in a gaseous with a high power laser[8]. If done correctly, this can be done without contamination of the nanoparticles.

The fabrication methods which will be attempted in this work are the reduction of HAuCl_4 and AgNO_3 using $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$, as well as the microwave-assisted reduction $\text{Ag}(\text{NH}_3)_2\text{NO}_3$. The chemical reduction process used requires a source of heat and so microwave heating will be compared with conventional heating to see how the particles differ. The particles produced via these methods will have their extinction spectra analyzed in order to understand their optical properties as well as obtaining qualitative information about their structural properties. The dimensions of the particles will be determined with an analysis of the Brownian motion of the particles in water[9].

2 Fabrication methods

A number of different methods were employed to create gold and silver nanoparticles. The methods involved the reduction of a metal salt in a solution to the metallic substance itself. This reduction requires heat and therefore several heating methods were tried.

2.1 Gold nanoparticles - chemical reduction

The first method employed was the chemical reduction of chloroauric acid (HAuCl_4) using sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) in an acidic environment (created by adding HCl). In order to do this, stock solutions of HAuCl_4 , $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ and HCl were prepared, at concentrations of $10^{-3} \text{ mol dm}^{-3}$, $7 \times 10^{-4} \text{ mol dm}^{-3}$ and $2.5 \times 10^{-2} \text{ mol dm}^{-3}$ respectively. The HAuCl_4 is light sensitive and to minimize light exposure the container was wrapped in aluminum foil.

The stock solutions were then used to make a number of different final solutions, in order to examine the effect of the concentration of each reactant on the process. Water was then added to these final mixtures, with a final volume of 10 cm^3 . An overview of the final concentrations of the reactants in the solutions is shown in tables 1, 2 and 3. These solutions were placed in boiling water for a total of five minutes, at which time the reduction was assumed to have reached completion. A study shows that the reaction is complete after four minutes[10], but this boiler seemed to have problems and the heating was prolonged to be certain that the reduction was complete. During heating, the solution gradually turned dark red which is a proof that colloidal gold had indeed been formed. The gold suspensions formed in this way were also assumed to be light sensitive, so the containers with the solutions were wrapped in aluminum foil.

Reports have shown that it is important to avoid contamination of the glassware used[11], and so after each synthesis, the glass used was rinsed in concentrated HCl and then with millipore water and left to dry. The HCl will not dissolve any gold residue in the glassware, but it is assumed that all the gold was in suspension and could therefore be rinsed out.

Table 1: The final concentrations in the solutions for the initial experiment.

Sample	HAuCl_4 ($10^{-4} \text{ mol dm}^{-3}$)	$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ ($10^{-3} \text{ mol dm}^{-3}$)	HCl ($10^{-4} \text{ mol dm}^{-3}$)
1	0.5	10	1.4
2	1	21	2.8
3	1	16	2.8
4	1	21	2.1
5	1	21	3.5
6	1	26	2.8
7	1	16	3.5
8	1	26	2.1

Table 2: The final concentrations of the solutions prepared for the second series of production of gold nanoparticles.

Sample	HAuCl_4 ($10^{-4} \text{ mol dm}^{-3}$)	$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ ($10^{-4} \text{ mol dm}^{-3}$)
1	2.5	3
2	2.5	4
3	2.5	4
4	2.5	5

The particles prepared here were then characterized using the methods described in section 3 in order to determine their sizes. The results are presented and discussed in 4.1.1.

Table 3: The final concentrations of the solutions prepared for the gold nanoparticles used for aggregation experiments.

Sample	H ₂ AuCl ₄ (10 ⁻⁴ mol dm ⁻³)	Na ₃ C ₆ H ₅ O ₇ (10 ⁻⁴ mol dm ⁻³)
1	2.5	2
2	2.5	4
3	2.5	6
4	2.5	2
5	2.5	4
6	2.5	6

Table 4: The final concentrations of the solutions prepared for the silver nanoparticles for both microwave heating and conventional heating.

Sample	AgNO ₃ (10 ⁻³ mol dm ⁻³)	Na ₃ C ₆ H ₅ O ₇ (10 ⁻³ mol dm ⁻³)
1	0.75	16
2	1	16
3	1.25	16
4	1	12
5	1	16
6	1	20

2.2 Silver nanoparticles - chemical reduction

The process used for the preparation of gold nanoparticles was also used to prepare silver nanoparticles, with AgNO₃ as a starting point. The final concentrations of the solutions used can be seen in table 4. Additionally, in order to study the differences between conventional heating and microwave heating, reduction of silver nitrate using sodium citrate was also carried out in the microwave.

To provide a better comparison, a series of measurements was carried out in which a solution was split in two and one half was heated in a water bath, while the other was heated in the microwave. In order for the solutions to have similar heating curves, the microwave was initially set to the highest power level, and when the solution reached the boiling point it was turned down to the lowest power level. The different concentrations of the reactants used for this experiment can be seen in table 5. No attempt to cool the solution in the microwave was made.

2.3 Microwave-assisted synthesis of silver nanoparticles

The next fabrication method involved the microwave-assisted reduction of Ag(NH₃)₂NO₃ to metallic silver. Recent studies indicate that this reduction can occur without the need for any additional reducing agent. One proposed mechanism for this is that the microwaves split H-radicals from water molecules. These powerful reducing agents then reduce the silver nitrate to metallic silver.

Table 5: The final concentrations of the solutions prepared to investigate the difference between conventional heating and microwave heating.

Sample	AgNO ₃ (10 ⁻⁴ mol dm ⁻³)	Citrate (10 ⁻⁴ mol dm ⁻³)
1	4.5	3
2	6	3
3	7.5	
4	9	3
5	7.5	3
6	7.5	3



Figure 1: The result of heating wet thermal paper in the micro-oven. Three distinct maxima can be seen as dark spots on the paper. The one labelled A was used for the synthesis process.

2.3.1 Characterization of the microwave.

The attempted synthesis was carried out in a commercial microwave oven, OBH NORDICA type 7514, with a power rating of 700 W. The microwave worked in a pulsed manner with a total cycle length of 30 s. The power setting of the microwave only influenced how long the microwave pulse lasted. This could be varied from 5 s to 30 s.

The electric field inside such an oven is not uniform, so measurements were carried out to characterize it. The synthesis was then performed where the characterization indicated that the field was strongest.

The field intensity was measured using thermal paper, which responds to heat by changing color. This was done by wetting the thermal paper uniformly and covering the plate of the microwave with it. Then, with the turntable deactivated, the microwave oven was turned on and kept on until the first color change was observed in the thermal paper. The resulting map of the field strength gave a very good indication as to where the field was strongest in the plane of the paper. An example of the map obtained can be seen on figure 1. There are three intensity maxima on the thermal paper, corresponding to the three dark spots. This experiment was carried out a number of times in order to confirm that the location of the maxima did not vary with time, and the results were consistent. During the synthesis the apparatus was placed at the highlighted maximum labeled A.

2.3.2 Synthesis

Before the synthesis started, the $\text{Ag}(\text{NH}_3)_2\text{NO}_3$ solution was freshly prepared. This was done by dissolving 1 g of AgNO_3 in 29.5 ml of water, creating a stock solution of AgNO_3 with a concentration of 0.20 mol dm^{-3} . 2.5 cm^3 of this was then placed in a conical flask and drops of concentrated ammonia solution were added. Tan precipitates immediately formed, and the addition of ammonia was continued dropwise until the precipitates vanished, indicating that all the silver was present as dissolved $\text{Ag}(\text{NH}_3)_2\text{NO}_3$.

This solution was then placed in the microwave oven and heated for several minutes (different attempts used different times). The microwave oven was used at the lowest power setting, corresponding to an average power output of 120 W. This meant that a working microwave pulse of 5 s was produced every 30 s.

In order to better understand the importance of non-thermal effects of the microwaves on the water, the synthesis was carried out multiple times using different cooling methods. Initially, the $\text{Ag}(\text{NH}_3)_2\text{NO}_3$ solution was merely placed in the microwave with no additional cooling. Next, the solution was placed in a water bath, in order to shield it from some of the microwave power. The water bath also acted as a cold reservoir, ensuring that the solution was heated slowly. Finally, a cooling system using silicone (which is completely unaffected by microwaves) passing around the solution was set up. A diagram of this setup can be seen on figure 2. As a control, the $\text{Ag}(\text{NH}_3)_2\text{NO}_3$ solution was heated in a water bath without the intervention of microwaves at all.

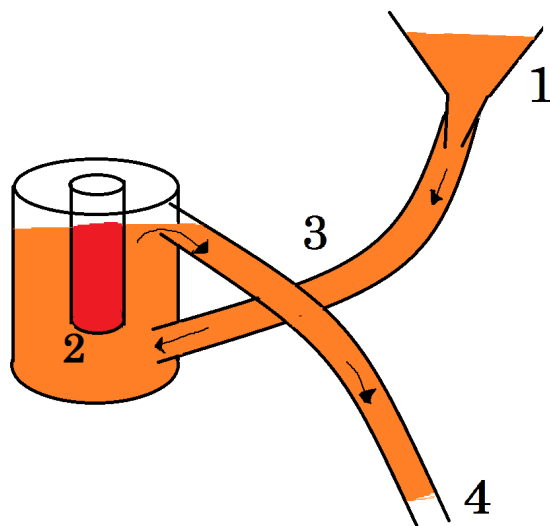


Figure 2: A diagram showing the silicone cooling system used to cool the $\text{Ag}(\text{NH}_3)_2\text{NO}_3$ solution. 1. Cold silicone flowing in, 2. silicone running past the special container with the $\text{Ag}(\text{NH}_3)_2\text{NO}_3$ solution cooling it, 3, gravity moves the silicone around, and 4. the silicone can be collected and reused.

These different setups allowed determination of the exact influence of microwaves on the reduction of $\text{Ag}(\text{NH}_3)_2\text{NO}_3$. The silicone based cooling system was a simple gravity-powered cooling system, as shown in figure 2.

- 1. Silicone is poured into a small reservoir, here a small funnel.
- 2. The silicone is flowing around the solution, cooling it.
- 3. Gravity pulls the silicone around in the system due to the difference in height of the funnel and the exit.
- 4. The silicone can be collected and poured into the funnel again for longer runs.

When the microwave was used at the highest power setting, this system was not sufficient to keep the solution from boiling. Due to the small volume of the reaction chamber (ca. 5 ml), this was not acceptable: Too much of the $\text{Ag}(\text{NH}_3)_2\text{NO}_3$ solution boiled away. However, at the lowest power setting, the solution was kept at a significantly lower temperature with the silicon cooling system that it was without.

3 Characterization methods

Once the metal nanoparticles have been created, it is of vital importance to be able to accurately characterize them, both in terms of their structural properties (size and shape), and in terms of their optical properties. These properties are of course intimately connected. The characterization is done by measuring the extinction spectrum of the particles in an aqueous solution, using a UV-visible spectroscopy, and by analyzing the Brownian motion of the particles (this method works on all small particles of spherical shape).

3.1 Extinction spectra

The nanoparticles created will interact with electromagnetic radiation because of the plasmon resonance. They will therefore have a very interesting extinction spectrum. The nanoparticles effectively block light at certain wavelengths from passing, thus producing their distinctive color. Some of the different colors they can have are shown in figure 3, here are shown three gold nanoparticles, where one shows two different aggregation states, and a range of different silver particles.

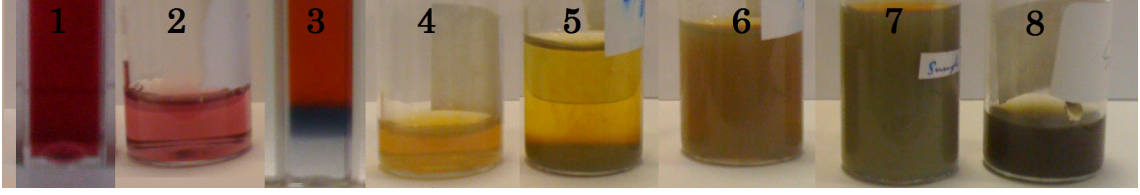


Figure 3: The different colors that nanoparticles may have. Container 1, 2 and 3 have gold nanoparticles, 3 has a layer of NaCl(aq) in the bottom. This forces some of the particles to cluster and this can be seen in the small blue layer.

Precipitates can be seen in some of the silver solutions; these could be removed by shaking, as is shown solutions 6, 7 and 8 in figure 3.

This color effect depends on the plasmon resonance which in turn depends on the physical properties of the nanoparticles. Therefore, by examining the extinction spectrum, it is possible to gain some information about the structural properties of the nanoparticles. This is done using a UV-vis spectrophotometer.

The extinction spectrum of a sample is caused by two separate effects, absorption and scattering. In the spectrophotometer used, the sum of these effects is measured (as absorbance), and it is not known how much of the extinction effect is caused by absorption and how much by scattering. Absorption is when the energy of the electromagnetic radiation is taken in (absorbed) by the sample. Scattering is when a photon collides with a sample molecule and propagates in a different direction after the collision. Both of these effects mean that the intensity of radiation passing straight through the sample decreases. The overall effect can be characterized by the absorbance coefficient, A , defined as

$$A = -\log_{10} \left(\frac{I_0}{I_1} \right), \quad (3.1)$$

where I_0 is the intensity of the incident radiation, and I_1 is the intensity of the transmitted light. For dilute solutions, the absorbance follows the Beer-Lambert law and can be expressed as $A = \sigma l N$, where σ is the cross-section of the material¹, l is the path length of the radiation. For spherical nanoparticles and N is the number of particles per unit volume. For spherical nanoparticles, the cross-section has been determined[12], and is governed by the relations

$$\sigma_{\text{extinction}} = \sigma_{\text{scattering}} + \sigma_{\text{absorption}}, \quad (3.2)$$

$$\sigma_{\text{absorption}} = \frac{8\pi^2 r^3}{\lambda} \left| \text{Im} \left(\frac{\tilde{\epsilon} - \epsilon_1}{\tilde{\epsilon} + 2\epsilon_1} \right) \right|, \quad (3.3)$$

$$\sigma_{\text{scattering}} = \frac{128\pi^5 r^6}{3\lambda^4} \left| \frac{\tilde{\epsilon} - \epsilon_1}{\tilde{\epsilon} + 2\epsilon_1} \right|^2, \quad (3.4)$$

where r is the radius of the particle, λ is the wavelength of the radiation, $\tilde{\epsilon}$ is the complex dielectric constant of the sphere² and ϵ_1 is the real dielectric constant of the surroundings. It can be seen that the absorption and scattering cross sections are at a maximum at the wavelength for which $\tilde{\epsilon} = -2\epsilon_1$, which corresponds to the surface plasmon resonance peak. Additionally, it can be seen that as the radius of the particles increases, the contribution from the scattering cross section starts to dominate, as it depends on r^6 and the absorption cross section depends on r^3 . For the small spheres we are looking at, however, absorption is the main contribution to the extinction cross-section.

Experimentally, the analysis of the sample solutions was very simple. The sample to be analyzed was placed in a cuvette and then into the spectrometer, in this case a Cary 1E UV-visible Spectrophotometer. A sample of pure³ water was placed in the spectrometer as well, so the spectrum of water could be subtracted from the final results. In order to be able to compare the results between different measurements, cuvettes with a path length of 1 cm were used for every measurement.

¹A measure of the probability of interaction.

²This is a function of wavelength

³millipore water with R 18 M Ω .

The machine then shone monochromatic light through the sample at 0.5 nm intervals and used the transmitted intensities to calculate the absorbance at each wavelength.

For gold nanoparticles Wolfgang Haiss et al. have provided a table in [11] (shown in appendix A) which can be used to easily find the size of the particles based on the extinction spectra. Assuming the particles to be roughly spherical and homogeneously distributed in the water, the important parameters are the absorption of the particles at the surface plasmon resonance (SPR) peak, and at 450 nm. The ratio between these two values uniquely determines the size of the nanoparticles. This works because the shape of the extinction spectrum does not vary significantly based on the size of the nanoparticles. The main parameters which vary are the position of the SPR peak and the height of the peak compared to the concentration. At a wavelength of 450 nm, the extinction is almost independent of the size of the particles and can therefore be used to account for the concentration of the gold nanoparticles. Knowing this, it is possible to find the size.

A similar technique is not possible in connection with silver nanoparticles, because there is no point in the spectrum where the extinction does not depend on size. Without this information, it is impossible to account for the concentration of the particles, and hence the size cannot be found. The extinction spectra can still be used for qualitative information about the particles. For example, a broad SPR peak indicates a broad size distribution.

It is also possible to obtain information about the aggregation state of the particles from the extinction spectra. When the particles form aggregates, the primary SPR peak will show a marked decrease and a secondary peak appears in the near-infrared region. If these aggregates grow sufficiently big, the particles will precipitate and a small layer can be seen on the bottom of the container. This happens to both gold and silver nanoparticles.

3.2 Brownian motion

Another technique for determining the size of small particles is the analysis of the Brownian motion of the particles. Brownian motion is the random movement of small particles in a gas or fluid caused by the collisions between the particle and the molecules of the fluid. It has been shown that this movement is dependent on the size and shape of the particle, the viscosity of the fluid and temperature [9]. If the size is known, then the Brownian motion of a particle can be used to determine the shape of the particle. If the shape is known, then the size can be calculated. An expression for the average displacement of a spherical particle is

$$\langle r^2 \rangle = \frac{2k_B T}{3\pi \eta a} t,$$

where k_B is the Boltzmann constant, T is the temperature in Kelvin, η is the dynamic viscosity, a is the radius of the sphere and t is time.

By measuring this average displacement over a certain length of time, it is possible to obtain accurate estimates of the size of the particles. The NanoSight NTA 2.0 was used for this purpose. In this machine, a holder for the sample is placed under an optical microscope. The holder shines light on the sample which is then scattered by the particles. The scattered light is recorded by a conventional CCD camera and is exported to a computer; the particles show up as white dots. The software for NanoSight then analyzes the movie, by finding the center of each white dot in every frame and calculating how it moves between frames. This allows the mean squared displacement, and hence the size, of the particles to be determined. The software has to be sure that it follows one particle, hence it can not have two particles' paths crossing. To prevent this, the software eliminates particles that are close to each other. The definition of 'close' depends on the setup of the program. The smaller the particle size, the larger is this distance. This means that small particles take up a lot of space and get eliminated against each other. Therefore, small particles cannot be detected reliable with this software. It is possible to increase the number of frames per second, causing the required distance between two particle to diminish and thus giving the software the ability to detect smaller particles, down to a size of ca. 15 nm.

The final results are shown in a histogram like the one in figure 4, giving an average size of the particles and the standard deviation. The graphs produced have been normalized so that they represent the probability density function of the size of the particles. The cumulative probability is 100 %.

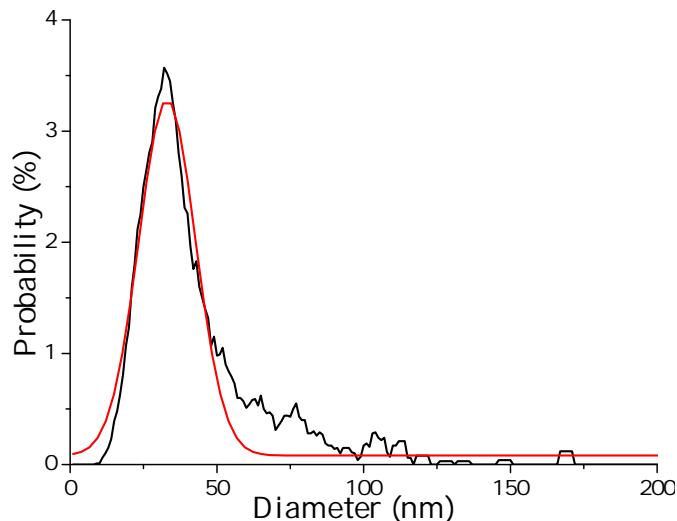


Figure 4: The result from a Brownian measurement of the second sample from table 3.

4 Results

The results of the experiments performed are many samples of gold and silver nanoparticles which have been characterized by the methods of the previous section. In this section, the extinction spectra of both silver and gold nanoparticles are examined first. Next, the effects of microwave heating is opposed to heating on a hotplate are examined. Then the stability and light sensitivity are examined and finally Brownian motion is used to determine the sizes of both gold and silver nanoparticles and the sizes of the gold nanoparticles are compared with those obtained using UV-vis spectroscopy.

4.1 Extinction spectra

As discussed in section 3.1 the small metal particles have very interesting optical properties, based on SPR. This is used to show what happens when the particles form aggregates, and to provide information on the size of the gold nanoparticles.

4.1.1 Gold

Spectroscopic analysis of the gold particles resulted in very characteristic extinction spectra with a sharp peak at roughly 520 nm. The exact position and shape of the peak varied based on the parameters used in the fabrication of the particles. The extinction spectra give one of the fastest ways of determining the size of the nanoparticles.

The extinction spectra of the samples from table 1 are shown in figure 5 and the resulting sizes are shown in table 6. The four samples shown in figure 6 have the same ratio of HAuCl_4 to $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$; they only differ in the amount of HCl added to the solution. It can clearly be seen that these ratios of reactants give relatively small nanoparticles, with sizes around 10 nm. In general, the extinction spectra of the particles produced in this series are very similar, as is the final size of the particles produced.

From figure 6 it can be seen that the concentration of HCl does not have a significant impact on the reaction. One possible effect is that larger concentrations of HCl might give rise to a wider size distribution of particles, but there are not enough data to say anything about this possibility. Another possibility is that HCl only affects the *rate* of the reaction, which would be irrelevant for the experiments carried out here. Due to the fact that the reduction process occurred without the presence of HCl, and that the size distribution of the particles produced seemed narrower in the absence of HCl, it was not used in subsequent syntheses.

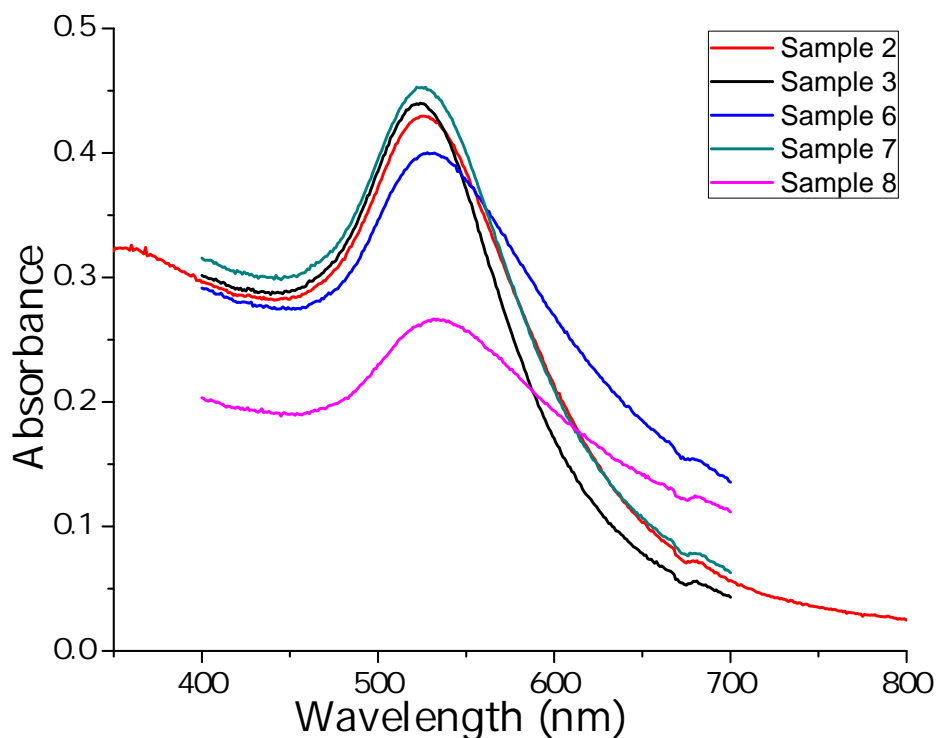


Figure 5: UV-vis spectra from some of the samples in table 6, the ones omitted out have the same ratio between gold and citrate as sample 2 and are shown in figure 6. Sample 6 and 8 have a "shoulder"; the absorption only drops slowly after the peak. This indicates that the nanoparticles in these solution are either aggregated or have an uneven size distribution. The small drop around 675 nm is almost certainly an artifact caused by an error in the machine.

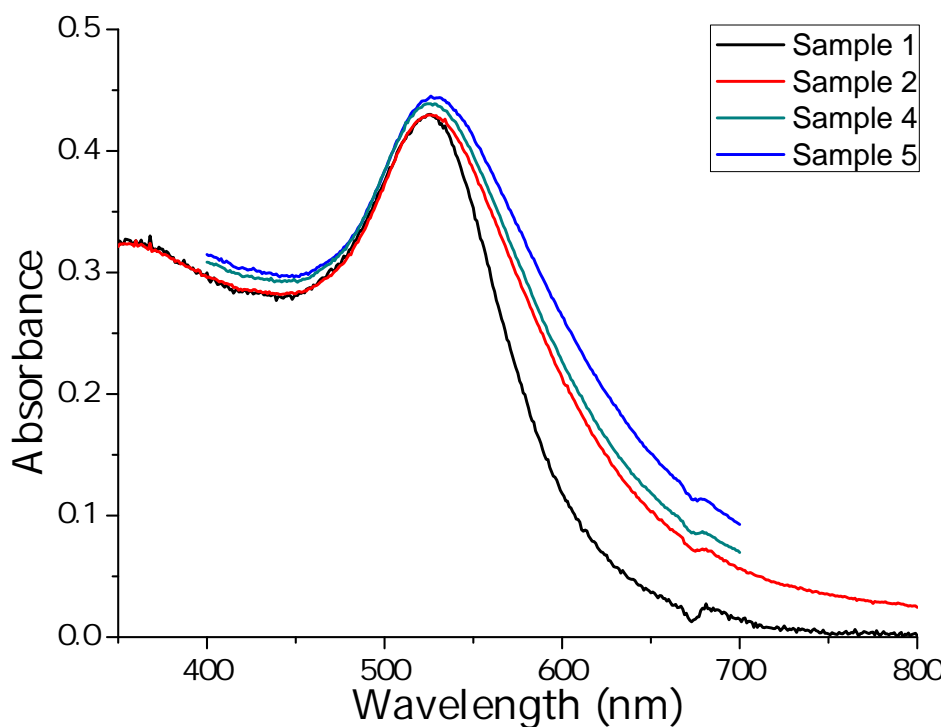


Figure 6: UV-vis spectra from the samples in table 6 with the same ratio between HAuCl_4 and citrate. The absorbance values of sample 1 have been multiplied with 2 to account for the fact that the solution was twice as dilute. The only difference between the sample is the amount of HCl, here it seems that more HCl gives broader size distribution.

Table 6: The ratios between the highest absorption(A_{high}) and the absorption at 450 nm(A_{450}) is used to get the size of the GNP[11].

Sample	A_{high}/A_{450}	Approx. Size(nm)
1	1.53	11
2	1.52	10-11
3	1.53	11
4	1.5	10
5	1.49	9-10
6	1.46	9
7	1.51	10
8	1.40	7-8

In the samples from table 2, smaller concentrations of sodium citrate and larger concentrations of chloroauric acid were used. The extinction spectra of these particles can be seen on figure 7, and the sizes this gave rise to are shown in table 7.

In general, the particles produced in this series of experiments are much bigger than others; with sizes ranging from 25 nm to 40 nm. This supports the results that lower concentrations of sodium citrate lead to larger gold nanoparticles, as has been seen in the literature[4].

Figure 7 also provides an estimate of the uncertainties associated with the reduction process. Samples two and three have the same concentrations of all reactants and have been treated in the same way, and yet give rise to different extinction spectra. Additionally, sample four should not have had the same extinction spectrum as sample three. There is no simple explanation for this deviation other than inherent error in the process.

Table 7: The ratios between the highest absorption(A_{high}) and the absorption at 450 nm(A_{450}) is used to get the size of the GNP.

Sample	A_{high}/A_{450}	Approximate Size (nm)
1	1.96	40
2	1.83	25-30
3	1.78	20-25
4	1.78	20-25

The relationship between the size of the gold nanoparticles and the concentrations of the reactants is shown on figure 8. It can be seen that in general the size of the nanoparticles increases as the ratio of HAuCl_4 to $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ increases. The relationship appears to be roughly linear in the range studied, and a regression line has been added to the plot. The equation of this is $y = 44x + 8.4$, showing that the size of the nanoparticles produced is very sensitive to the concentration of the reactants. The coefficient of determination is reasonably high, at $R^2 = 0.85$, but the data set is too small for the trend to be absolutely clear. More studies would have to be performed, within the range studied here as well as outside it, to gain a better understanding of the exact relationship.

4.1.2 Aggregation

The extinction spectrum of the gold nanoparticles has a sharp peak around 520 nm. The aggregation state and the size distribution of the particles determines how this peak looks. If the particles form aggregates, then the peak will be smaller around 520 nm and a secondary peak will form in the red to near-infrared band. This has been tested by adding NaCl to a solution of nanoparticles and measuring how the extinction spectrum changed over time. The NaCl changes the surface potential of the particles, making them attracted to each other. This causes them to form aggregates. After the addition of salt, distinct layers tend to form. An example of these can be seen on figure 10. Because of these layers, it has been necessary to stir the solution before each measurement to ensure accuracy. For this series of measurements, a fast but less accurate spectrophotometer was used, Red Tide 650USB from Ocean Optics, in order to be able to capture the extinction spectra with sufficiently high frequency.

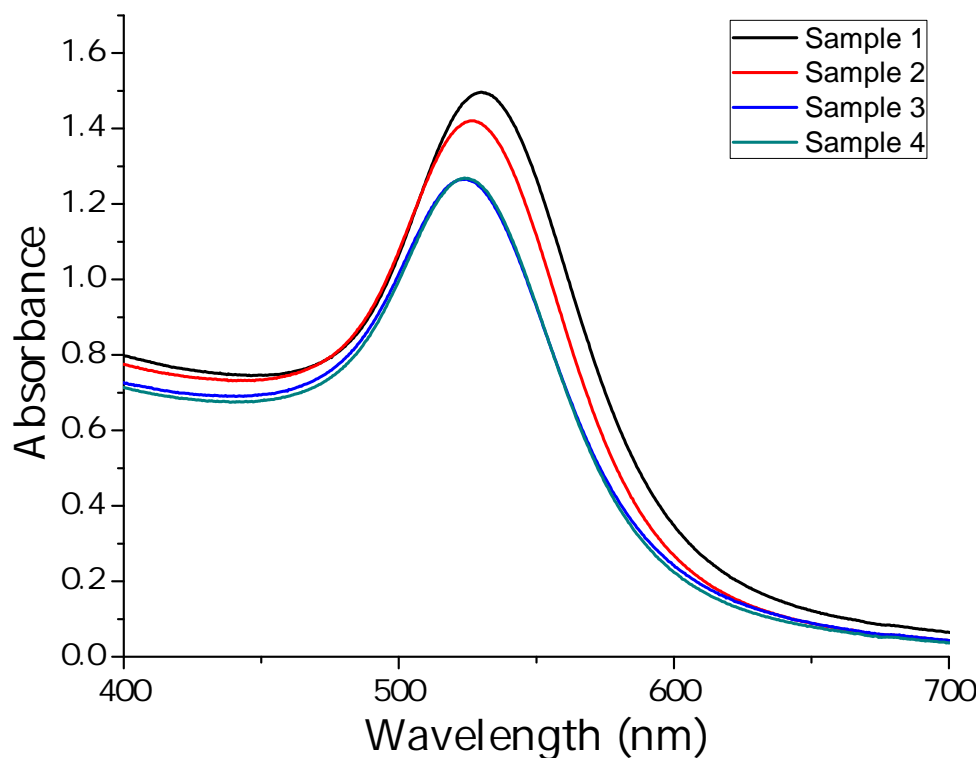


Figure 7: UV-visible spectra for the samples in table 7, with the sizes of 20 to 40 nm. Notice that there is no shoulder here. This means that the particles are monodisperse and have not formed aggregates. Sample 3 and 4 are almost identical.

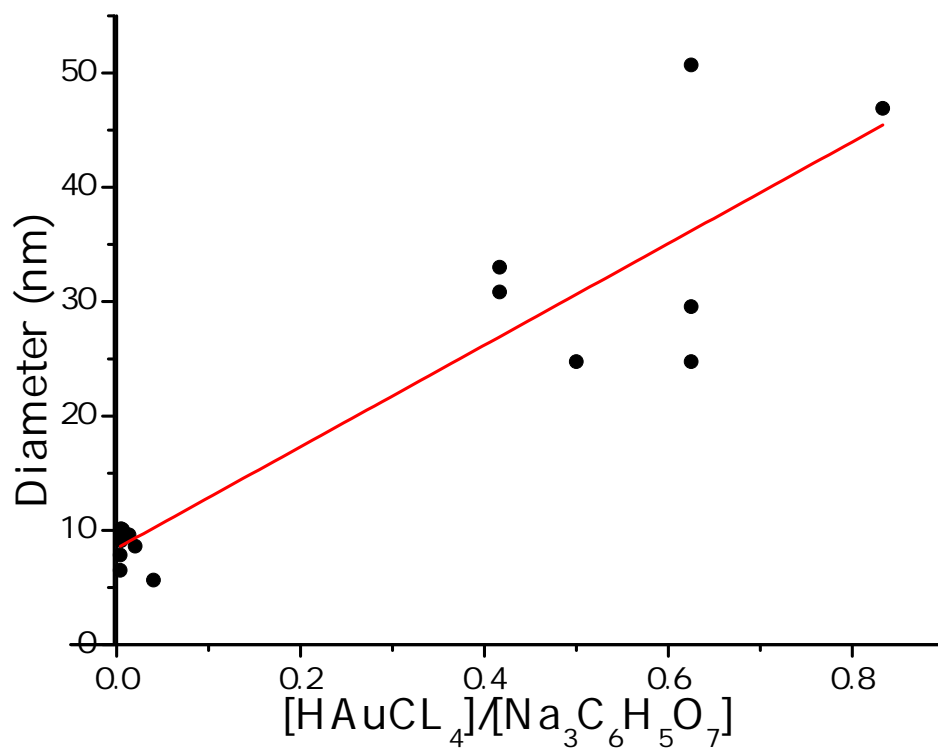


Figure 8: A graph of the relationship between the size of the nanoparticles produced and the ratio of the reactants. The linear regression line has the equation $y = 44x + 8.4$, and the coefficient of determination is $R^2 = 0.85$.

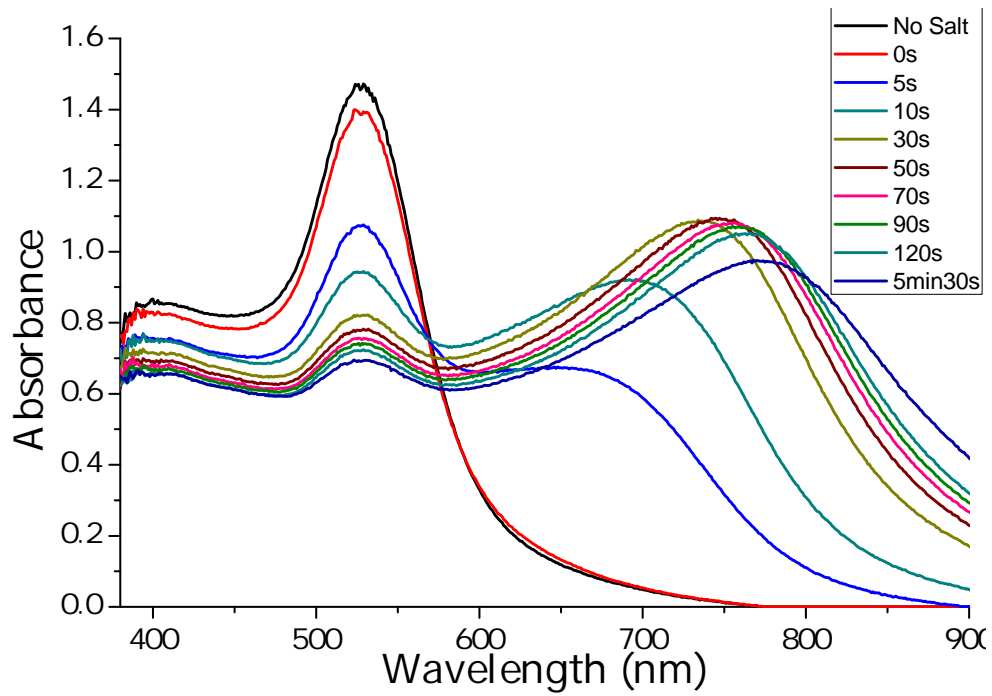


Figure 9: UV-vis spectra for sample 1 from table 7. NaCl has been added to the solution and the particles start to form aggregates and, over the course of roughly five minutes, the absorbance rises in the interval 650 – 900 nm.

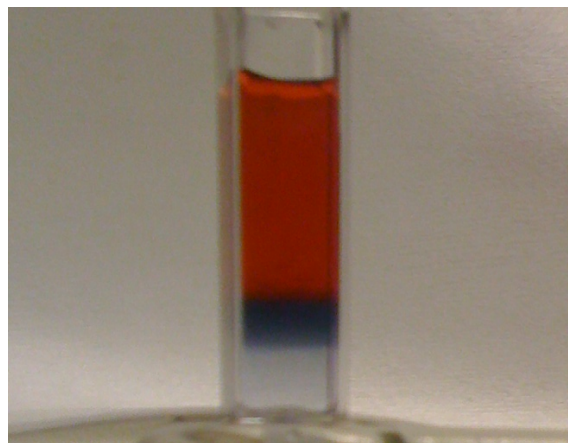


Figure 10: A visible separation into layers of the gold nanoparticles after NaCl has been added.

This spectrometer suffered from a defect, as it was possible to slightly misalign the cuvette, leading to large differences in the extinction spectrum. Therefore, when the mixture started to separate into layers, a glass rod was used for stirring in order to disturb the arrangement as little as possible. This system is assumed not to contaminate the solution.

Sample 1 from table 2 was used to perform the measurements. 100 μl of 0.25 mol dm^{-3} NaCl were added to a cuvette containing 2.5 ml of the sample and the extinction spectrum was measured frequently. The spectra from after the addition of salt have been corrected for the fact that the particles have been diluted by a factor of $\frac{26}{25}$. Additionally, the changes to the extinction spectrum which occurred over the course of one measurement are considered negligible.

The spectra obtained from this procedure are shown in figure 9. It can be seen that the peak at 520 nm is quickly reduced and a broad peak in the near-infrared emerges. The reaction takes place over the course of roughly five minutes. When the solution is left to stand for longer time (two hours in this case), the aggregates become so big that they start to precipitate out of suspension, forming a black layer of particles that is clearly visible to the naked eye. This process is not reversible, and so if the gold suspension is to be used for further work, care has to be taken not to expose it to compounds like NaCl which could cause such a transformation.

4.1.3 Silver

The only fabrication method of silver which resulted in nanoparticles was the chemical reduction of silver nitrate using sodium citrate. This reduction process was performed with both conventional and micro-wave heating, and the spectra of the particles this gave rise to are presented in this section. Discussion of why it was not possible to carry out the reduction of silver nitrate using only the microwave oven and of the differences between the two heating methods will be done in section 4.2.2.

The fabrication of silver nanoparticles via chemical reduction proceeded in much the same way as that of gold nanoparticles. The same factors seem to govern the size of the nanoparticles produced, in that lower concentrations of sodium citrate produced generally larger particles. There were however a number of differences. Firstly, the size distribution was in general much broader for the silver nanoparticles than it was for the gold nanoparticles. This was clearly seen as a wide peak in the extinction spectra, in the Brownian motion measurements (see section 4.4) and by the fact that the silver solution appeared cloudy and muddy instead of clear and green/yellow. Extinction spectra for silver can be seen in figure 11. Some of the silver appeared clear and yellow, e.g. silver 1 on the graph, and some appeared cloudy and muddy, e.g. silver 4.

4.2 The effect of microwave heating

4.2.1 Gold

As one important parameter in the synthesis of gold nanoparticles seems to be the temperature at which the reduction takes place, experiments were carried out to compare the two heating sources. Three pairs of samples were created and heated in different ways. The results can be seen in figure 12. The original spectra are not the same, because a lot of water boiled away in the micro oven, making the final solution more concentrated. From the corrected graphs, it can be seen that the nanoparticles produced in the microwave have the same extinction spectrum as those heated on a hot plate. This means that the particles produced are also identical. The reaction in the microwave oven occurred faster than the one on the hot plate, probably because the micro oven caused very strong, localized heating.

4.2.2 Silver

The difference between heating the solutions in a microwave oven and on a hot plate proved very important for the chemical reduction of silver nitrate. While gold was readily reduced in a conventional heater in water just below the boiling point, the silver was not. The reaction occurred very slowly on a hot plate, and in some cases failed to occur at all.

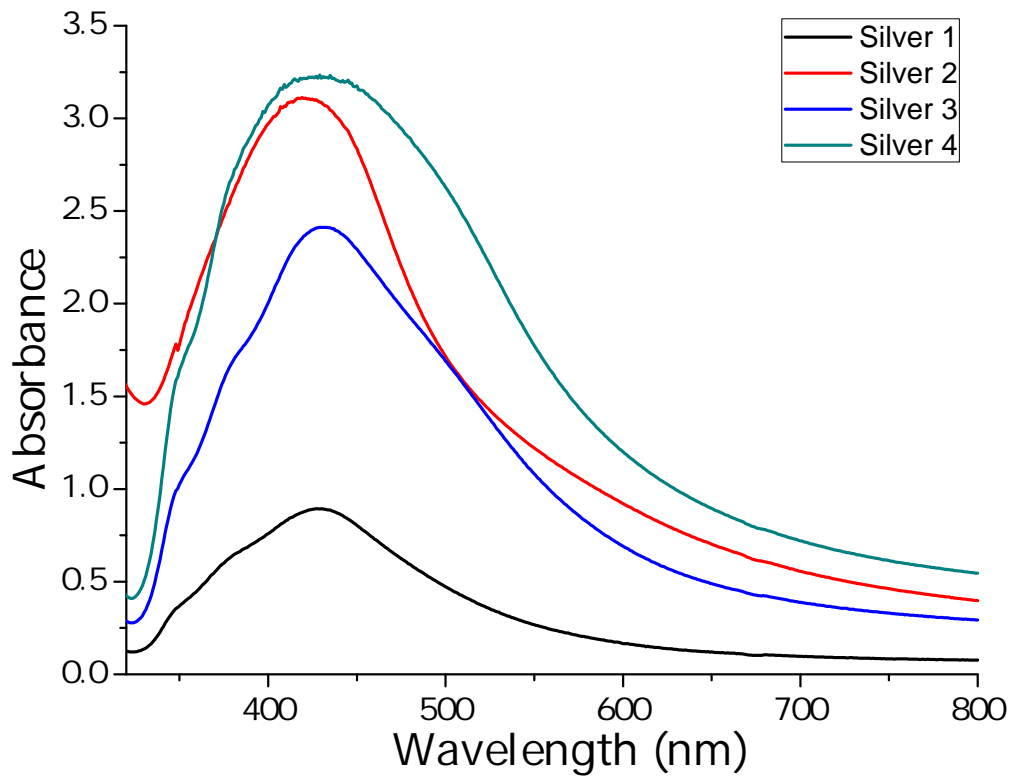


Figure 11: UV-visible spectra from the different samples of silver nanoparticles. End results ranged from clear yellow in color to dark muddy and cloudy.

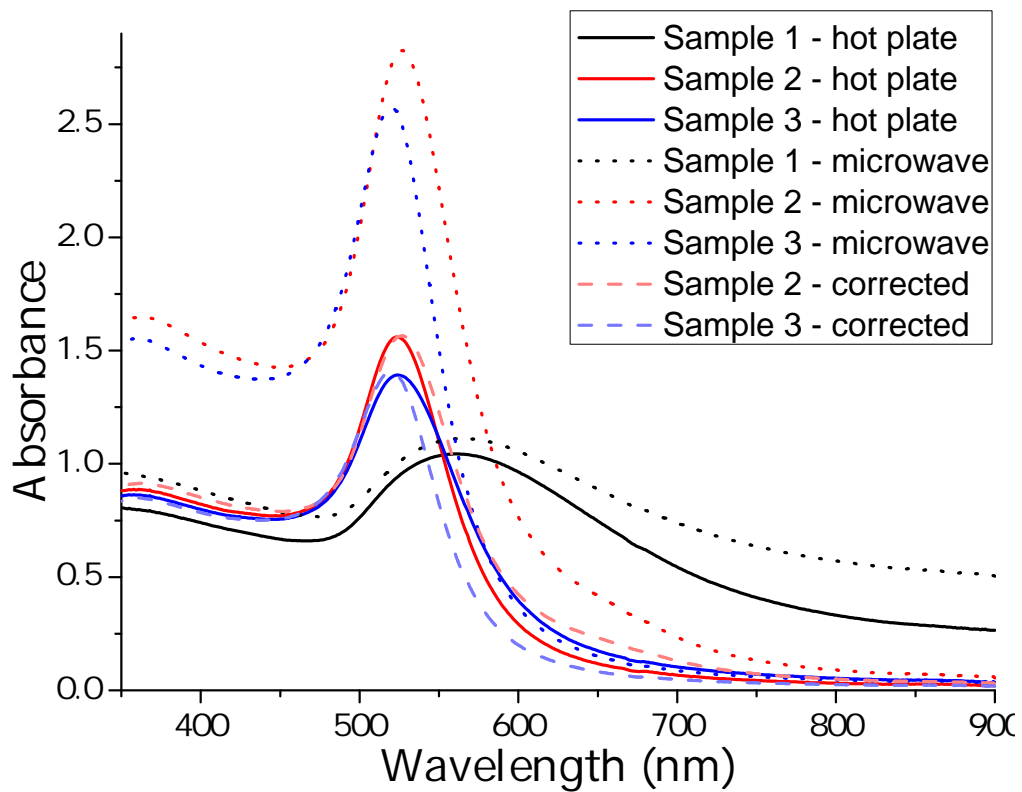


Figure 12: Several sample of gold nanoparticles heated in different ways. The corrected graphs for sample 2 and 3 take the differences in volume into consideration.

This is where using a microwave to heat the solution proved to be more reliable than using a hot plate, in that the microwave successfully heated the water quickly and delivered enough power to a localized area that the solution was kept at a vigorous boil for the duration of the heating progress. Using microwave heating, the reduction reaction occurred rapidly and reliably.

The microwave-assisted synthesis of silver nanoparticles proved harder to carry out. Previous results indicate that a solution of $\text{Ag}(\text{NH}_3)_2\text{NO}_3$ could be reduced to metallic silver under microwave irradiation without the need for additional reducing agents[5]. This proved not to be the case in the experiments performed here. When NH_3 was added dropwise to a solution of AgNO_3 , colored precipitates formed and then disappeared, indicating that the desired reaction was occurring and that $\text{Ag}(\text{NH}_3)_2\text{NO}_3$ had indeed formed. When the resulting solution was heated in a microwave oven, no reaction was observed regardless of the duration of the microwave irradiation. One possible explanation for this difficulty is that the AgNO_3 solution is unstable over time, and hence was not pure when the microwave synthesis was attempted. This seems unlikely however, given that chemical reduction of the AgNO_3 was still possible when it was attempted several days later.

The microwave-assisted reduction of silver was attempted again without the cooling system and with significantly higher power dissipated to see if any reaction occurred. The result was a liquid containing black specks which were significantly bigger than the 10-100 nm that were expected. Attempts were made to identify the black substance, but they were not successful. At no stage was the green color which is characteristic of silver nanoparticles observed. The results in [5] could not be reproduced.

4.3 Stability

In order to determine how the properties of the nanoparticles produced were affected by the exposure to light and time, several of samples were deliberately left uncovered for approximately 5 days. The extinction spectra were measured both before and after. There was a slight change in the spectra; a little more "shoulder" was observed. This shows that the particles cluster together, but after leaving them exposed for longer durations of time, nothing more happened. Additionally, when the silver nanoparticles were allowed to stand for a number of weeks, it was observed that the nanoparticles precipitated out of solution, indicating that the colloid is not entirely stable over time. This occurred even though the particles had not been exposed to light.

4.4 Brownian motion

In general the Brownian motion measurements gave an easy way to measure the size of the particles. One thing which must be noted is that the system used was not able to track particles smaller than roughly 15 nm which means that it was not possible to obtain useful measurements for the smallest particles produced.

4.4.1 Gold

The Brownian motion measurements were performed for all the samples, but only the largest particles gave usable results, because the smallest particles were too small to be picked up by the machine. In the results obtained, the sizes given by this technique are in close agreement with the values obtained from the spectra. Figure 13 shows the results from sample 1 table 7. The Gaussian fit gives the size 37.5 nm with $\sigma = 9.4$ nm. This is close to the value found earlier, as seen in table 7. The small bumps in the area 90 - 200 might be due to several particles that have clustered. The size distribution of the gold nanoparticles fits the value found by using the extinction spectra. This agreement indicates that the nanoparticles *can* be described by the model used to generate the table in appendix A. In table 8, the size for gold nanoparticles found from Brownian motion and from the spectra analysis can be seen. The sizes fit with ± 10 nm as the maximum error. This error can be caused by the fact that the particles are non monodisperse and that the shape is not a perfect sphere as both techniques assumed. The fact that they are close to each other means that the assumption of the shape is a good one and only slight variations of the shape exists. These slight variations have different impacts on the two different characterization techniques. Additionally, to the size estimate from analysis of the spectra is very sensitive to the value of A_{high}/A_{450} . A small error here can produce a very large error in the size.

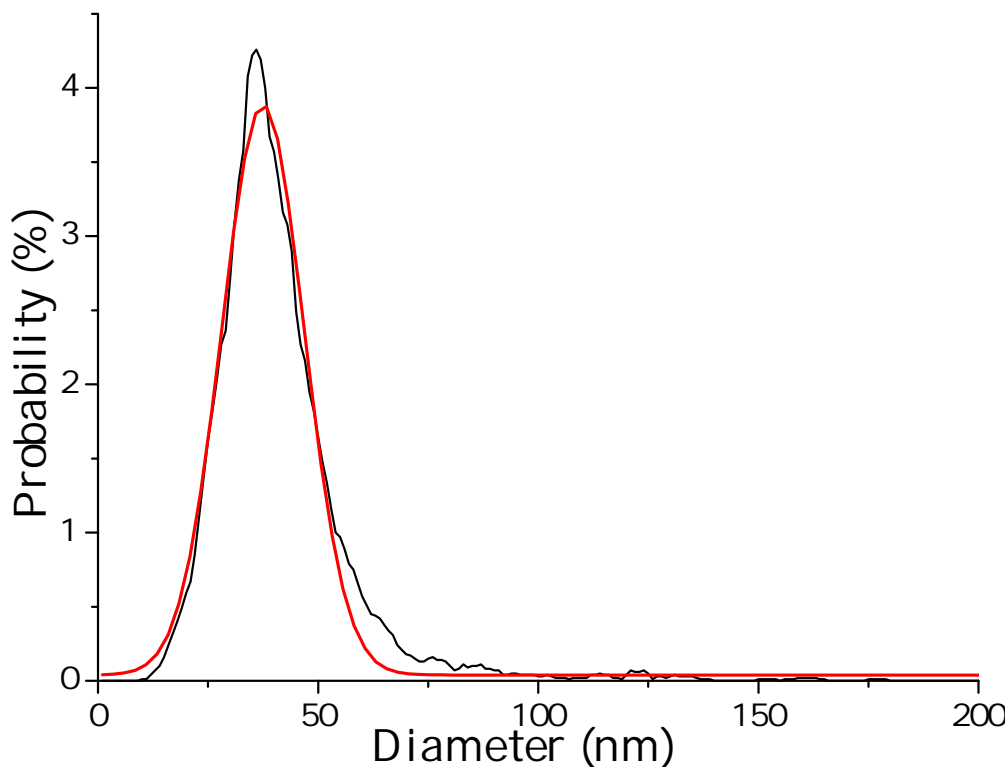


Figure 13: The size distribution of gold particles in sample 1 from table 7. The Gaussian regression show that the peak is located 37.5 nm at and $\sigma = 9.4$ nm. This is close to the value that found in

Table 8: The sizes for gold nanoparticles found from the UV-visible spectra and from the Brownian motion. A difference of maximum 10 nm, is observed, which might come from non monodisperse particles and different particles shapes than assumed. The in general, close agreement between the two methods can be seen.

Sample	Size from Brownian morion (nm)	Size from spectra(nm)
1	37.5	40
2	35.1	25-30
3	27.1	20-25
4	34	20-25

4.4.2 Silver

The silver nanoparticles produced were large enough to be clearly detected by the machine. The Brownian motion measurements of these were therefore accurate and, assuming the particles are spherical, so is the resulting estimate of the size and size distribution. The graph for the size distribution of the silver nanoparticles can be seen in figure 14. The Gaussian fit finds the mean value to be 34.2 nm. There are no data to compare this to, because the UV-vis spectra cannot be used to estimate the size of silver nanoparticles. One of the other samples created gave a much wider peak which can be seen in figure 15. This sample has a wider peak, with a mean of 30 nm and the standard deviation of 12.5 nm. The peak appears split, and it is not known if this is due to a measuring error in the system or if there actually are two separate peaks.

The different techniques used to calculate the sizes of the nanoparticles generally agree with each other. This means that for gold nanoparticles, the method described in [11] can be used to accurately establish the size of monodisperse gold nanoparticles based on simple UV-vis spectroscopy. These are very fast and the machines for this are readily available.

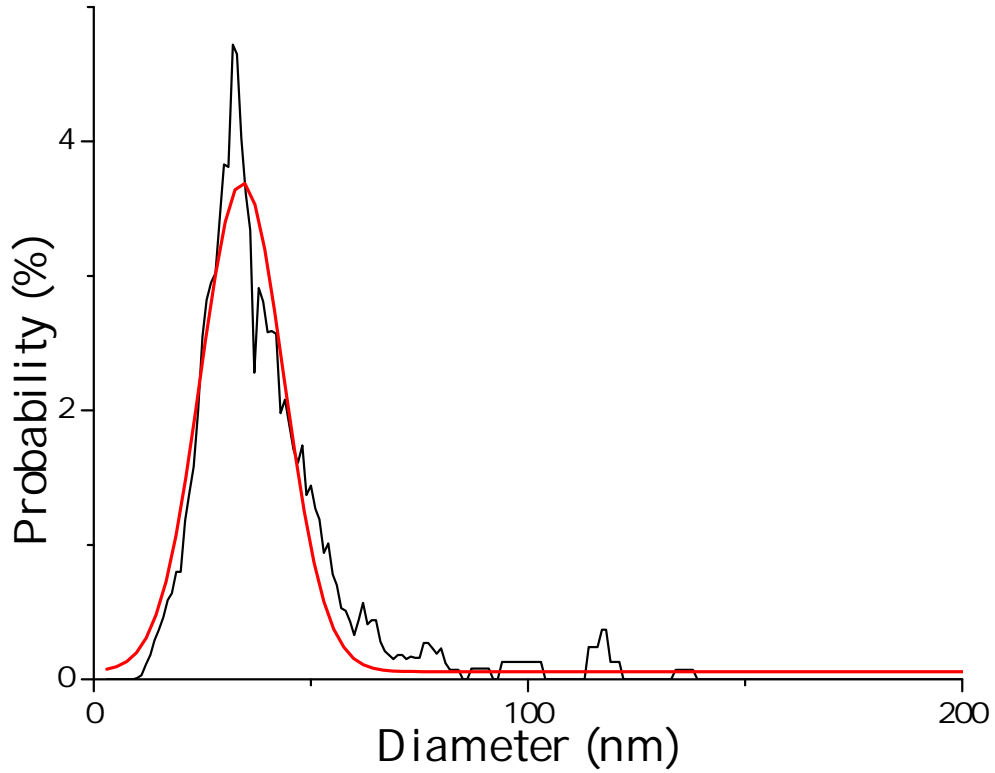


Figure 14: The size distribution of silver particles of the first sample from table 4. The Gaussian regression show that the peak is located at 34.2 nm and $\sigma = 9.5$ nm.

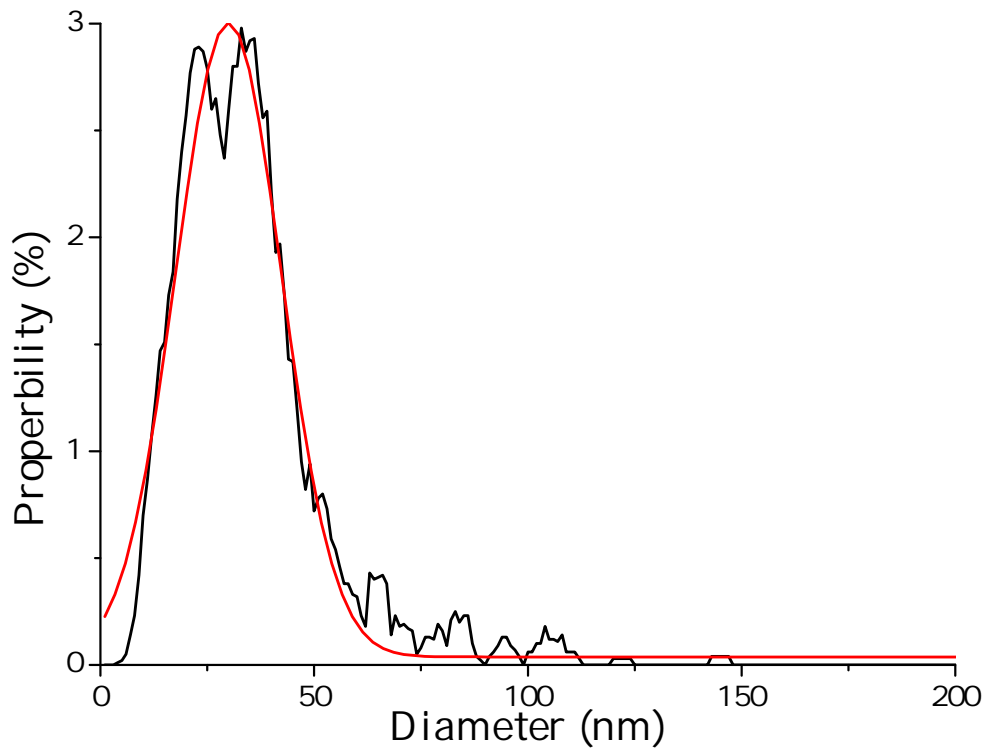


Figure 15: The size distribution of silver particles of the third sample from table 7. The Gaussian regression show that the peak is located at 30 nm and $\sigma = 12.5$ nm. The split in the peak may results from a maesurement error or indeed the nanoparticles

5 Discussion

Inherent in any process are sources of error which make the results obtained less reliable. The possible sources of error in the synthesis and characterization process will be discussed in this section. Next, the potential uses of the nanoparticles, both in research and in society as a whole will be presented. Finally, a brief overview will be given of what further work is needed to better understand the metal nanoparticles and which could prove useful.

5.1 Sources of error

There are two main areas of the experiments performed which could be affected by errors and hence give inaccurate results. These are the synthesis process and the characterization. Errors in the synthesis would lead to the production of nanoparticles that were different from what was expected. Reports in the literature suggest that contamination of the glassware could lead to unwanted nucleation and later unwanted aggregation of the nanoparticles [11]. Even though the glassware used was not cleaned perfectly between each synthesis and therefore must have been contaminated to some degree, this was not observed. Measuring uncertainties in the synthesis process are assumed to be negligible. Scales correct to within 1 mg were used to measure out amounts of ≈ 0.5 g, an error of less than 0.2 %. The pipettes used to measure volumes also have a negligible error

The main source of error in the synthesis process is therefore the potential contamination of the glassware used to hold the liquids. The synthesis process should therefore be fairly reproducible.

For the characterization, the uncertainties involved become more significant. The CARY spectrophotometer used had a uncertainty of $\pm 0.07\%$, which is acceptable. The OceanOptics spectrophotometer had a significantly higher uncertainty, which is important because for gold nanoparticles there is an exponential relationship between $\frac{A_{\text{high}}}{A_{450}}$ and the size of the nanoparticles. A small error in this ratio can cause a huge error in the estimated size of the particle. The Brownian motion measurement has a statistic uncertainty, so as many particles as possible should be used for each measurement. By the law of large numbers, the mean size of the sample should then converge towards the actual mean.

5.2 Applications in society

It is already possible to buy nanoparticles at very affordable prices. In these production processes, the synthesis is scaled up and performed in large containers, heated directly without a water bath are used. Another way could be to use a stronger reducing agent, thus eliminating the need for the heating step. This might contaminate the nanoparticles and require a cleaning process. Sometimes the contamination of the nanoparticles is acceptable, eg. if the optical properties of gold nanoparticles in the interval 400-600 nm are needed and citrate is the reducing agent. Citrate is only optically active in the interval 200-300 nm and would therefore not interfere with the results in the longer wavelengths.

The large scale production of the particles opens up for wider use in the society. The optical properties can be used for eg. filters for specific wavelengths, enhance medical imaging techniques and other detection equipment. Which gives a much better chance at diagnose cancer and other diseases early. The catalytic abilities can enhance many other processes in industrial manufacturing, diminishing the cost and time required.

For the wide use of nanoparticles in the society the toxicity of nanoparticles has to be known in detailed. For most cases every nanoparticles should be tested as a completely new drug [13], as the toxicity of the particles cannot be determined *a priori* based only on knowledge of their structure.

According to the literature, gold particles are non-toxic and can be inserted into living cells without harming them directly or indirectly⁴. Studies have tested some nanoparticles and several have come out with positive results. So the nanoparticles can be used in medicine; gold nanoparticles have been used to reduce joint pain in rats[14], and medicine carriers[15].

Silver nanoparticles have anti-bacterial properties and are used in some places to disinfect wounds[3].

⁴For example by acting as a catalyst for a harmful reaction

5.3 Further work

In this report we have seen that there is a correlation between $[\text{HAuCl}_4]/[\text{Na}_3\text{C}_6\text{H}_5\text{O}_7]$ and the size of the particles. Further work should be done to understand the exact relationship between the ratio of the reactants and the sizes, as well as attempting to extrapolate the data set to see what occurs at higher or lower ratios. Once this is done, spherical gold nanoparticles of a specific size will be much easier to produce directly, which will be very useful.

The exact nature of the interactions of HCl with the other reactants involved in the formation of gold nanoparticles should also be studied. In this work it appears that the presence of HCl during the reduction of HAuCl_4 causes the particles to form with a larger size distribution (indicated by a broad peak in the extinction spectrum of the particles). This is generally undesirable, but understanding why the effect occurs, and to what extent, could make it possible to create particles with a very narrow size distribution.

The microwave-assisted reduction of silver nitrate is another area requiring more study. The failure of the work done here to reproduce the results in the literature indicate that there are more complex factors at play in the process. A better understanding of the mechanism by which microwaves can bring about the reduction would help understand these factors. Additional attempts to bring about this reduction should also be made, in order to establish under what circumstances, if any, it occurs.

This is especially advantageous in the reduction of silver nitrate using sodium citrate which occurs very slowly at low temperatures (and is in general difficult to carry out in a water bath). Further studies should definitely be made in order to identify how microwaves can influence the reduction of silver nitrate and to better understand the conditions required for the effect to occur.

6 Conclusion

In the experiments performed here, it has been established that the most important parameter which controls the size of the nanoparticles produced via the chemical reduction process is the ratio of metal salt to sodium citrate in solution. Lower relative concentrations of sodium citrate lead to larger particles, while higher concentrations lead to smaller particles. The relationship between size and relative concentration appears roughly linear in the range studied. By varying the concentration, it has been possible to create gold particles of sizes ranging from 10 to 40 nm and silver particles in the range 30 to 40 nm. Larger sizes are possible to produce by using even lower concentrations of sodium citrate, however these results appear less reproducible. When the concentration of sodium citrate is below a critical level⁵, the reduction reaction no longer produces non-aggregated homogeneous spherical particles, as can be seen from the extinction spectrum. This means that in order to produce large spherical particles the ratio of $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ to HAuCl_4 in the solution should be around 0.6-0.8 : 1.

The reduction processes carried out will not occur spontaneously at room temperature, and so a heating system is required. A microwave system was tested and it was seen that in the case of gold, the particles produced in the microwave are identical to the ones produced using conventional heating. For the chemical reduction of silver nitrate, the microwave oven proved more effective as a source of heat than the hot plate. With the microwave heating, the reduction reaction occurred rapidly and reliably, while with conventional heating the reaction occurred in a much slower manner and in some cases did not occur at all. The microwave proved better at delivering very strong, localized heating.

The particles produced were shown to be spherical and monodisperse, as evidenced by the close agreement between the size of the gold nanoparticles obtained through spectroscopic analysis, and that obtained by Brownian motion measurements. The particles were also stable over time and under exposure to light.

It was not possible to reproduce the microwave-assisted reduction of silver nanoparticles using no additional reducing agents, despite trying a variety of different setups.

⁵when the ratio of sodium citrate to chloroauric acid drops below 0.8

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A Gold nanoparticles: size determination

Table 9: The table that was used to determine the different sizes of gold nanoparticles[11].

A_{spr}/A_{450}	d/nm	A_{spr}/A_{450}	d/nm	A_{spr}/A_{450}	d/nm
1.10	3	1.56	12	1.96	40
1.19	4	1.61	14	2.00	45
1.27	5	1.65	16	2.03	50
1.33	6	1.69	18	2.07	55
1.38	7	1.73	20	2.10	60
1.42	8	1.80	25	2.12	65
1.46	9	1.86	30	2.15	70
1.5	10	1.92	35	2.17	75