AN INVESTIGATION INTO THE COLLOIDAL STABILITY OF SILVER NANOPARTICLES PRODUCED IN ETHANOL MICRO-JETS

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The preparation of nanoparticles in liquids is a challenging task. To immerse metal atoms into liquids, chemical reduction methods are typically employed. Whilst such methods are able to produce a wide range of nanoparticles, the technique is restricted by the need for soluble starting materials, and they often produce excess chemical waste. The novel, and globally unique method of sputtering atoms into a liquid jet, developed by the University of Leicester, allows the even dispersion of any metal / semi-metal atoms into any liquid in a clean and controlled environment, thus clearly overcoming these restrictions. This project’s aim was to determine how the concentration of water present in an ethanol solution affected the colloidal stability of the silver nanoparticles that formed in the liquid jet solution. By modifying the experimental set-up, the purity of the samples was improved by an order of magnitude, allowing water to be reintroduced in a controlled manner. Through ultra-violet and visible light spectroscopic analysis of a range of samples produced under various conditions, it was concluded that water fundamentally affects the reactions that occur, and the nanoparticles that form. The results from this investigation show that in the absence of water, silver nanoparticles, produced by sputtering silver onto a liquid ethanol jet, undergo an avalanche-type reaction, which causes the clusters to lose their stability in solution, exhibited by the disappearance of the surface plasmon feature from their UV-Vis spectra over time. In contrast, in the presence of water, the nanoparticles are apparently more stable, and in particular retain their plasmon resonance for prolonged periods. This is a result that may be of great interest for the practical use of metal nanoparticles produced in solution, particularly for plasmonic applications.
To my beloved grandmother, Ann, who believed I could achieve anything,

my fantastic family, Caroline, Lydia and Nick, for their continued support, even when it
took me a year to finish,

and my beautiful girlfriend, Raquel Azuaga Vera.

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LIST OF ABBREVIATIONS

LASIS – Laser Ablation of Metal Targets Synthesized in Solution

SMAD – Solvated Metal Atom Dispersion

JOD – Jet-Only-Deposition

JCD – Jet-Co-Deposition

TEM – Transmission Electron Microscopy

UV-Vis – Ultraviolet-Visible Light

HPLC – High Performance Liquid Chromatography

XTM – Crystal Thickness Monitor
1 INTRODUCTION

Due to their distinctive size-dependent properties, nanoparticles are at the forefront of many technological advances (Eustis and El-Sayed, 2006; Hosokawa, 2012). They are currently being used, and evaluated for use, in a wide range of applications in fields such as electronics, medicine and engineering (Lohse and Murphy, 2012). For example, nanoparticles can be used to create smaller, higher performance components, benefitting consumer devices such as computers or mobile phones (Lohse and Murphy, 2012). Medical applications include detecting diseases and caging molecules (Dreaden et al., 2012), which can assist in the specific targeting of damaged cells; an exciting prospect in the quest to cure cancer. Nanostructures are also often considerably stronger than bulk materials in some environments, and are therefore used in areas such as structural engineering; carbon nanotubes are used for reinforcement purposes (Sau et al., 2010). Silver (Ag) nanoparticles are of particular interest due to their array of favourable properties. They are highly conductive (Alshehri et al., 2012), highly thermally conductive (Iyahraja and Rajadurai, 2015) and have high optical reflectivity (Umadevi and Jegatha Christy, 2013). Consequently, their synthesis and corresponding properties have been extensively studied over the past decade, leading them to be the most widely used material in nanotechnology consumer products (Sun, 2013). For instance, silver nanoparticles are used for their antibacterial properties in medical and consumer products such as anti-bacterial coatings for medical devices and household antiseptic sprays (Xiu et al., 2012). Water filters incorporating silver nanowires have been shown to be very efficient for cleaning water that is polluted with bacteria (Schoen et al., 2010). Silver nanoparticles are also traditionally used to catalyse important industrial reactions.
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including oxidation of ethylene to ethylene oxide, propylene to propylene oxide and methanol to form aldehyde (Nagy and Mestl, 1999). Due to their high electrical and thermal conductivities, silver nanoparticles are also widely used in electronics industry as conductive fillers in conductive adhesives and thermal interfacial materials. Most recently, two-dimensional random networks of silver nanowires have been exploited to serve as transparent conductive films. These networks are much more mechanically flexible than traditional doped metal oxide conductive films, such as tin-doped indium oxide, due to the thin diameters of the silver nanowires, creating exciting prospects for consumer touch screen devices (Sun, 2013). As well as such commercial uses, because of their optical properties, silver nanoparticles are also relevant to the popular research field of plasmonics. Silver nanoparticles exhibit strong and broad surface plasmon resonances in ultra-violet and visible light, due to a strong coherent oscillation of free surface electrons in the nanoparticles, resulting in strong absorption and scattering of incident light. The unique surface plasmon resonances in silver nanoparticles benefit their traditional use in catalytic oxidation reactions (for example ethylene epoxidation, and CO oxidation) because excitation of the plasmon resonances on the surfaces of silver nanoparticles form energetic electrons that transfer to the chemical species, allowing the temperature of such reactions to be lowered, hence leading to an increase in energy efficiency and long-term stability (Christopher, Xin and Linic, 2011). Just these few applications of silver nanoparticles that have been discovered to date, illustrate the diversity, and thus importance, of nanoparticle use in modern society. The potential that they represent means that it is crucial we continue to develop better methods of producing them, which allow us to better control their size, shape, purity and stability.

Nanoparticles are often produced in liquids; this is because liquids have a high density, which promotes the opportunity for atoms and molecules to combine to form nanoparticles more readily than, for example, if they were in the gas phase. One such common, and general method of synthesising nanoparticles in liquids is via the precipitation or co-precipitation of metals or metal compounds from super-saturated aqueous solutions (Cushing, Kolesnichenko and O’connor, 2004). Sondi et al., (2003) reported manufacturing silver nanoparticles with an average diameter of 26.3 nm ± 7.4 nm by reducing aqueous silver nitrate (AgNO3) solutions with ascorbic acid in the presence of Daxad® 19 (polynaphthalene sulfonate, supplied as a sodium salt).
As silver monomers precipitate out of solution via reduction, and begin to grow into nanoparticles via Ostwald ripening (the phenomenon where smaller particulates are effectively consumed by larger ones) Daxad® 19 serves to passivate the surface of the nanoparticles preventing them from agglomerating to form macroscopic constituents. Such surfactants are typical in chemical reduction processes, facilitating the production of colloidally stable nanoparticle solutions. Their use, however, has the drawback of blocking the surface of the nanoparticle for interaction with other species (Smetana, 2006). They may also change the chemical nature of the particle themselves and interfere with catalysis on the surface of the nanoparticle. In fact, Yonezawa et al., (2000) showed that surfactants can even affect the size distribution of nanoparticles. It was shown that when aqueous AgNO₃ was reduced by sodium borohydrate, NaBH₄, in the presence of TADDD (bis(11-trimethylammonioundecanoylaminoethyl)disulphide dibromide) the size distribution of the resultant nanoparticles varied with the ratio of stabilizer that was used in the reaction. Mean diameters of 4.8 nm were reported for TADDD/Ag = 0.2, compared to mean diameters of 3.3 nm for TADDD/Ag = 5.0. In this case, excess borohydride reduces the disulphide to a thiol that serves as the surfactant or “capping ligand”. These silver nanoparticles, however, are amongst the smallest reported in literature for chemical reduction techniques (Cushing, Kolesnichenko and O’connor, 2004).

It has also been reported that silver nanoparticles can be precipitated from non-aqueous solutions. Pastoriza-Santos and Liz-Marzán (1999) demonstrated that N,N-dimethylformamide (DMF) could serve to reduce silver perchlorate, AgClO₄, whilst also passivating the resultant precipitates to form silver nanoparticles of between 6 nm to 20 nm in diameter. In this experiment it was also shown that size of the nanoparticles could be tuned by adjusting the temperature of the reaction. The saline-based stabilizing agent (DMF) however, is susceptible to hydrolysis and condensation, particularly at elevated temperatures and as such, some of the silver nanoparticles exhibited silicon oxide coatings.

Another such powerful chemical reduction technique that is frequently used to produce silver nanoparticles involves the use of hot organic solvents. For example, hot oleylamine, cis-1-amino-9-octadecene, OAm, can be used for the rapid reduction of AgNO₃, to form multiply twinned icosahedral silver nanoparticles with diameters tunable in the range of 2 nm – 20 nm. The shape of such nanoparticles arises from the fact that
the reduction of silver ions in OAm is very fast, hence only nanoparticles with multiply twinned crystalline structures grow, forming only icosahedral shaped nanoparticles (Sun, 2013). If however, chloride ions are added to the solution, silver species nucleate through two different paths to form two different types of particles. Tang *et al.*, (2007) demonstrated that silver nanoparticles derived from AgCl are typically single crystal because the presence of chloride ions etch the metal twinning nuclei in the oxidative environment. Consequently, the AgCl nanocrystals that form are single crystal compared to the ones derived directly from AgNO$_3$, which are multiply twinned. Typically the multiply twinned nanoparticles, have sizes smaller than the single-crystal AgCl nanoparticles that form simultaneously, and therefore upon heating the system, the smaller multiply twinned particles are gradually dissolved via the growth process of Ostwald ripening. Sun (2013) reported using this process to grow single-crystal polyhedral in truncated nanocubes. Furthermore, Tang *et al.*, (2007) demonstrated that the crystallinity of a nanoparticle can have a direct effect on its properties. For example, single crystal silver nanoparticles were shown to form Ag$_2$Se nanoshells with a well-defined hollow cores when reacted with selenium, compared to multiply twinned silver nanoparticles forming single crystal Ag$_2$Se solid spheres.

As is evident from the examples listed, an exciting array of nanoparticles of different shapes, sizes and structures can be produced using chemical reduction methods. Nevertheless, they are restricted by their very nature. The production of each class of nanoparticle requires a unique, and often complex chemical reaction; and in some instances, the reduction of some metal ions (with standard electrode potentials greater than -0.481 V) are either not feasible or exceedingly difficult (Cushing, Kolesnichenko and O ‘connor, 2004). In addition, the process requires soluble starting materials, and there are many metals and semiconductors that are not naturally soluble. Furthermore, to limit agglomeration and make colloidally stable dispersions, the nanoparticles usually require capping ligands to passivate their surface, significantly reducing their purity and modifying their reactivity (Smetana, 2006). Lastly such methods often produce chemical by-products or residual ions (Amendola, Polizzi and Meneghetti, 2007) which pose a substantial disadvantage in applications such as surface enhanced Raman scattering spectroscopy (SERS) in chemical analysis (Procházka *et al.*, 1997). As a result, there are many limitations as to what can be achieved with chemical reduction techniques making the discovery of other production techniques desirable.
Physical methods for nanoparticle production disperse metal atoms in solution without the need for chemical precursors or reducing agents. For example, *Laser Ablation of Metal Targets Synthesised in Solution* (LASIS) is a technique that involves generating metal atoms in a small plasma plume from an ablated metal target, which then react with both the solvent and each other to form nanoparticles. Amendola *et al.*, (2007) report size distributions of 1.9 nm, with a standard deviation of 1.5 nm, for silver nanoparticles synthesised in acetonitrile; and 2.2 nm, with a standard deviation of 2.5 nm, for silver nanoparticles synthesised in DMF (by 9 ns pulsed-laser irradiation of a silver plate (1064 nm, at 10 J/cm$^2$)). In comparison to silver nanoparticles synthesised by the method of co-precipitation in DMF, which produced nanoparticles of 13.0 nm ± 3 nm in diameter (at room temperature) (Pastoriza-Santos and Liz-Marzán, 1999) the nanoparticles produced by LASIS were considerably smaller, thereby demonstrating the impressive potential of LASIS. Furthermore, in this experiment, Amendola *et al.*, (2007) proved that the silver nanoparticles could be manufactured free and colloidally stable, without the use of surfactant molecules, thereby vastly increasing the nanoparticles’ purity. The ablation method suffers, however, from low production yields; it is difficult to accumulate sufficient concentrations for various applications (Werner *et al.*, 2008). Another disadvantage is that the size distribution tends to be wide because the aggregation of ablated atoms and clusters is difficult to control; for silver nanoparticles synthesised by Amendola *et al.*, (2007) as shown above, the size distribution was 2.2 nm ± 114%. Additionally, in some instances, the long term stability of nanoparticles synthesised from LASIS are questionable, and hence it is sometimes necessary to utilise chemical stabilisers to overcome this problem (Werner *et al.*, 2008).

*Solvated Metal Atom Dispersion* (SMAD) is a physical nanoparticle production technique that involves producing an atomic metal vapour by sputtering or thermal evaporation, which is then co-deposited with solvent vapours onto liquid nitrogen-cooled walls (Stoeva *et al.*, 2002). It has the significant advantage over LASIS that gram quantities of nanoparticles can be produced in a single experiment (Smetana, 2006). Unfortunately, to synthesise colloidally stable nanoparticles, the use of capping ligands are still required, compromising purity. Further, Smetana (2006) reports that the size distributions of silver nanoparticles vary according to the choice of capping ligand used to passivate the surface of the nanoparticles. Size distributions of 6.0 nm ± 2.0 nm were
reported for spherical silver nanoparticles synthesised in 2-butanone coated with trioctyl phosphine (TOP) after 6 hours of digestive ripening (gentle heating until an equilibrium size is obtained) and 6.6 nm ± 1.0 nm spherical silver nanoparticles coated with dodecane thiol, compared to a population of polydispersed nanoparticles with mean diameters of approximately 14.0 nm (as estimated by UV-Vis spectroscopy) when stabilised with dodecyl amine, synthesised under the same conditions.

In this project, in order to explore the many promising aspects of physical production methods of nanoparticles in solution, nanoparticles were synthesised by mixing metal atoms directly with a liquid micro-jet; a production technique developed by the University of Leicester (Galinis and von Haeften, 2012; Youle and von Haeften, 2015; McNally, Galinis, Youle, Chantry and von Haeften, 2016). In this process, a micro-jet of solvent of 50 µm in diameter is introduced to a vacuum region, which then subsequently freezes on a liquid nitrogen-cooled surface or ‘cold trap’. Silver atoms are then sputtered onto the micro-jet which aggregate to form the rapid and clean production of nanoparticles in a single step. Based on similar principles to SMAD, the liquid jet technique has the ability to produce large yields of nanoparticles. In contrast however, nanoparticles produced by the liquid jet have been shown to be colloidally stable after a period of one year in the absence of stabilizing surfactant molecules (McNally, Galinis, Youle, Chantry and von Haeften, 2016). Due to a large degree of dispersion and mixing between the metal atoms and the solvent molecules, the technique also produces very small nanoparticles small diameter with narrow size distributions, 2.0 nm ± 0.7 nm without need for size selective techniques (McNally, Galinis, Youle, Chantry and von Haeften, 2016) because the same quantity of metal is dispersed over a greater number of nucleation centres (Baldyga and Pohorecki, 1995; Johnson and Prud’homme, 2003). Consequently, the liquid jet technique demonstrates enormous potential for rapid and economical production of clean nanoparticles. In the liquid jet technique, it is hypothesised the solvent molecules in which the nanoparticles are grow, passivate the surface of the nanoparticles, limiting their growth.

In 2012, it was shown that when metallic vapours are deposited onto liquid jets, nanoparticles form (Galinis and von Haeften, 2012). In 2015, investigations, conducted by myself, showed the size of these metal nanoparticles, in this case silver, correlated with the concentration of the silver in the sample (Youle and von Haeften, 2015). In the
case of high silver loading, produced by silver atoms co-deposited into an ethanol micro-jet and onto the corresponding freezing ethanol surface, in a process called jet co-deposition (JCD), the sizes, as imaged using transmission electron microscopy (TEM) fitted a log-normal distribution with a median diameter of 3.3 nm ± 1.4 nm. In samples produced by silver deposition solely onto the liquid ethanol jet itself, in a process called jet only deposition (JOD), i.e. low loading, the sizes of the resultant silver nanoparticles fit a log-normal distribution of 2.0 nm ± 0.7 nm, see appendix 1. Rarely have such small and narrow distributions of silver nanoparticles been reported for other physical synthesis techniques. As previously stated, in comparison, Amendola et al., (2007) report size distributions of 1.9 nm for silver nanoparticles synthesised by LASIS in pure acetonitrile, however they have a relatively wide standard deviation of 1.5 nm; and 2.2 nm, with a standard deviation of 2.5 nm, for silver nanoparticles synthesised by LASIS in DMF. For a direct comparison for the physical production of silver nanoparticles synthesised in ethanol, Werner et al., (2008) report silver nanoparticles of 33 nm in diameter were produced when 0.1 µm flakes of silver were ablated in ethanol. Consequently, as demonstrated, corresponding nanoparticles produced by the liquid jet not only have a narrower size distribution, but are also much smaller. Compared to LASIS, the liquid jet technique has the additional advantage that is a much cleaner and a more controlled process. To liberate atoms via LASIS, the laser is focused on a small target with a very high energy density, typically in the order of 100 GW pulsed sources, meaning it is also possible to ‘crack’, or break, chemical bonds in the surrounding solvent, compromising the purity of the nanoparticle samples. In contrast, in the liquid jet set up, the atom source is separate from the solvent source, so the purity of the resultant solution is much higher.

Another considerable advantage of the liquid jet technique over other physical production techniques is that it is possible to dissolve other molecules or even other nanoparticles in the solvent prior to firing the solvent into the vacuum. It therefore becomes possible to introduce sputtered metal atoms directly to a dissolved material in the jet with a high degree of mixing. In 2016, such an advantage was probed. It was also shown that the growth of silver nanoparticles was limited by the presence of pre-existing silica nanospheres (Mcnally, Galinis, Youle, Chantry and von Haeften, 2016). Atomic silver was deposited onto silicon nanospheres pre-dissolved in the ethanol micro-jets. TEM images of resultant samples, acquired by myself, showed that single clusters of
silver nanoparticles decorated the silica nanospheres, and that large nanoparticles (of sizes greater than 100 nm) which were observed in regular JCD and JOD samples, were absent. The conclusion from this work was that silver nanoparticles grew on the silica surfaces, and not prior to that, in the liquid. The size distribution of these silver nanoparticles on the silica spheres fit a log normal distribution of 4.6 ± 1.3 nm; slightly larger on average compared to those produced by JCD and JOD, but narrower in overall size distribution, due to the absence of the ‘large’ nanoparticles, appendix 2.

Via the liquid jet technique, because it is possible to restrict metal atoms from co-depositing onto the frozen solvent surface and only allow deposition onto the liquid micro-jet itself (JOD); for the first time, the liquid-jet technique also enables the investigation of what happens when metal atoms come into contact with the surface of a liquid. Consequently, as well as producing an exciting array of nanoparticles, the liquid jet technique creates new opportunities to study the fundamental reactions that occur at liquid, solid interfaces. In this investigation, we begin to probe the interaction that occurs between the metal atoms for the first time. It is hypothesised the interaction of the metal atoms with the solvent could affect the aggregation process, and as previously stated, it has been shown that nanoparticles produced via the liquid jet in JOD, and JCD, are colloidal stable up to one year after production. In all previous investigations however, the samples produced have been subject to significant contamination from water vapour that condenses on the liquid nitrogen cold trap prior to production. Consequently, one hypothesis is that the water, present in solution could be stabilising the nanoparticles. In this report, a particular effort was made to improve the purity of our nanoparticle samples, allowing the subsequent investigation to study the solvent-metal interaction, and the effect of water content on nanoparticle production. It was found that water has a profound effect on the colloidal stability nanoparticles produced in ethanol. This report presents the first systematic investigation into the effect of water on the nanoparticles produced by the liquid jet technique, assessed using ultraviolet and visible light spectroscopy.
2 Method

The quantity of water present in the samples produced via the liquid jet method in the previous investigations was $0.55 \pm 0.18$ ml, and hence the purity of all previous samples was $94.5 \pm 1.8\%$ ethanol, $5.5 \pm 1.8\%$ water (see section 4.1). Using a new experimental set-up, as described in the following sections, the purity of nanoparticle samples was improved, such that the samples contained only $0.2\%$ water. This allowed water to be re-introduced in known quantities, enabling the study of the effect water has on the colloidal stability of the nanoparticles. Systematic investigation using UV-Vis spectroscopy also revealed how the colloidal stability of the silver nanoparticles depends on the silver to solvent ratio, and by analysing different layers of the nanoparticle samples, it was revealed the liquid jet technique produces samples that contain numerous particles of differing density.

To produce nanoparticles using the liquid jet technique, a vapour of metal atoms was deposited onto a solvent micro-jet of $50 \mu$m in diameter, which subsequently freezes on the liquid nitrogen-cooled cold trap. The experimental set-up consisted of a custom-built liquid jet assembly mounted inside an Edwards Auto-306 vacuum thin film coater (a vacuum chamber with an argon ion sputter source) with a customised glass bell jar sealed to a cylindrical glass cold trap. The argon ion sputter source created the vapour of atoms; the liquid jet assembly allowed the introduction of a micro-jet of solvent to the vacuum environment; and the cold trap allowed the liquid template to exist in a metastable state for a number of minutes. Figure 1 shows the Auto-306 thin film coater with the argon ion sputter source, and customised glass bell jar (credit to Uwuigbe and von Haeften, 2016).
Figure 1: The liquid jet apparatus used to produce the nanoparticle samples (Uwuigbe and von Haeften, 2016). The apparatus, as labelled, are mounted to the Edwards Auto-306 thin film vacuum coater and encased inside the custom welded glass bell jar. Note, in this image, the liquid jet assembly is not mounted.

The Auto-306 vacuum coater is evacuated using a roughing pump, a turbo pump and a cryopump connected in series, and is controlled using the vacuum control panel. Pirani pressure gauges measure the pressure behind each pump and in the vacuum chamber. First, one uses the vacuum control panel to activate the roughing pump which achieves a low vacuum, or ‘rough’ vacuum of approximately $10^{-2}$ mbar. At this point, the turbo pump automatically engages and reduces the chamber pressure to approximately $10^{-5}$ mbar in approximately 5 minutes. At this point the pumping mode is manually switched from fine pumping to throttle pumping, and a consistent pressure of $1\times10^{-4}$ mbar is maintained in the chamber. It was noted that leaving the turbo pump to operate in fine
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pumping mode overnight achieved vacuums of approximately $10^{-7}$ mbar. This assisted the turbo pump’s ability to repeatedly pump down, which was necessary to make multiple nanoparticle samples in one day, and hence was considered good practice. Liquid nitrogen could also be poured into the cryopump to aid the roughing process; literally freezing gas molecules to the cryopump walls, further reducing the chamber pressure. This however, was only done when necessary, as gas molecules defrosting from the cyropump overnight would cause the more-effective turbo pump to fail.

Once a consistent chamber pressure of $1 \times 10^{-4}$ mbar was established, the custom-built cylindrical ‘cold trap’ was cooled using liquid nitrogen. Unlike previous investigations the cold trap in this investigation can be cooled from outside of the vacuum chamber by pouring liquid nitrogen into the inlet pipe (figure 1). In prior experiments, the cold trap was a stainless steel cylindrical column, which needed to be first cooled in liquid nitrogen and then transferred to the vacuum chamber. This allowed the opportunity for water vapour from the air to condense on the cold trap prior to the experiment, which would inevitably form part of the nanoparticle sample. In this investigation, because cooling is only applied after the vacuum has been established, water vapour cannot condense on the cold trap and contaminate samples. Consequently, the contribution from water that is present in the samples can be limited to that which is already dissolved in the high-grade pure ethanol, 0.2% (see section 4.1). Additionally, external cooling also yields the advantage that one can continually replenish the liquid nitrogen as it boils off, thereby maintaining a stable vacuum for longer; prolonging production time.

Next the argon ion sputter source was initiated. The pressure on the first BOC Edwards Argon canister was set to 1 bar, and ultra-pure argon was introduced via a needle valve across the surface of the sputter target, increasing the pressure in the chamber from $1 \times 10^{-4}$ mbar to $1 \times 10^{-2}$ mbar. A DC magnetron discharge was then ignited, generating an argon plasma at 600 V, 0.2 A, sputtering silver atoms from a pure silver target (99.99% purity, Kurt J. Lesker, Product No. EJTAGGXX403A2).
Sputter deposition is a well-documented process, whereby ionised gas (argon) atoms ‘bombard’ the surface of a target material, causing it to eject a ballistic vapour of atoms (Williams, 1979). The strong electric potential applied over the target material strips electrons from incident inert gas atoms (argon). The positive argon ions are then attracted to the negatively charged silver target (cathode) ‘smashing’ into it to release the atomic vapour, figure 2. At a distance greater than the diameter of the cathode target, the vapour is emitted radially in all directions (Maréchal, Quesnel and Pauleau, 1994). The positive argon ions recombine with the ever-present free electrons from the negative electrode to form neutral atoms, releasing photons in the process and hence the plasma glows a violet colour (characteristic to silver), see figure 5. At the operating pressure of $1 \times 10^{-2}$ mbar, the sputter source generated predominantly neutral silver atoms, with the expectation of producing a small percentage yield of silver ions and a maximum of 10% of 2-3 atom clusters (Gnaser and Oechsner, 1991). The deposition rate of the sputtered silver atoms was measured using a crystal thickness monitor (XTM) in the vacuum chamber (see figure 1). A quartz crystal in the XTM vibrates at its resonance frequency specific to its mass. As the sputtered metal atoms deposit on the quartz crystal, the accumulating mass decreases the resonance frequency of the crystal. The XTM then calculates the thickness of the material that has been deposited onto it using the change in frequency. Figure 3 shows how the deposition rate (thickness accumulating per time) of silver changes with sputter current, at a distance of 30 cm from the sputter target, for a vacuum pressure of $1 \times 10^{-2}$ mbar. It is noted the relationship between sputter current and deposition rate is quadratic. It is hypothesised this is because the sputter target heats up with increasing sputter current; the extra kinetic energy assists in ejecting atoms from the material surface.
Figure 3: Silver deposition rate as a function of sputter current at a vacuum pressure of $1 \times 10^{-2}$ mbar, as measured by the XTM, 30 cm from the sputter source. The relationship between sputter current and deposition rate is quadratic. It is believed this is because the sputter target heats up with increasing sputter current. The additional kinetic energy assists in ejecting atoms from the material surface.
Immediately after sputter deposition was initiated, the liquid ethanol jet was introduced to the vacuum chamber via the custom-built liquid jet assembly. The custom-built liquid jet assembly, shown schematically in figure 4, consisted of a 100 ml stainless steel reservoir (A) containing the solvent, with a customised *High Performance Liquid Chromatography Grade* (HPLC) fitting holding a 50 µm inner diameter fused silica capillary (C). This was mounted inside the vacuum dome of the Auto-306 coater prior to each experiment and connected to the second of two BOC Edwards ultra-pure argon canisters via a Swagelok® fitting (B). The pressure behind the liquid, was atmospheric, as it contained air. Due to the pressure difference between this, and the evacuated chamber, ethanol would occasionally leak from the 50 µm capillary, and deposit into the chamber. This would cause a temporary increase in pressure in the chamber as the liquid ethanol evaporated. Nevertheless, this effect was not significant enough to restrict the system from reaching vacuums of $10^{-4}$ mbar.

![Figure 4:](image)

Upon commencing the experiment, the valve on the BOC Edwards argon canister was opened, and the pressure behind the liquid was rapidly raised to 40 bar, forcing a micro-jet of solvent out of the 50 µm capillary (C), from which it traverses the vacuum chamber (D) before striking, and freezing on the cold trap. Consequently, at least for a short time, the experimental set-up allows a liquid template and a vacuum to co-exist. The solvent used in all of the samples presented in this report was ethanol (HPLC grade, Sigma Aldrich, Product No. 459828, CAS 64-17-5, 99.5% purity, 0.2% water). The solvent could be emptied and replaced after each experiment by opening the liquid inlet (E).
To vary the quantity of water present in each sample, solutions of known volumes of HPLC grade ethanol and ultra-pure water were pipetted into liquid jet reservoir prior to each experiment. The different concentrations used in this investigation were: 10% water, 90% HPLC grade ethanol; 1% water, 99% HPLC grade ethanol, and pure HPLC grade ethanol (which included 0.2% water).

During the experiment, sputtered silver atoms from the argon ion sputter source deposit into the liquid jet and onto the freezing solvent surface. Due to Rayleigh instability, under applied pressure, the flow of the jet breaks up into micro-droplets (Papageorgiou, 1995). This is important because if this was not the case, the solvent would freeze from the point where it strikes the cold surface back to the source. It is hypothesised that the silver atoms nucleate into small nanoclusters, which are then passivated by the solvent molecules. As mentioned previously, it is an advantage of the liquid jet technique that it can operate in two modes: JOD (jet-only deposition) metal atoms depositing only onto the liquid jet; and JCD (jet co-deposition) – metal atoms deposit onto both the jet and onto the frozen solvent surface with the jet. To eliminate JCD and only operate JOD, one simply blocks the line of sight between the sputter source and the cold trap with an aluminium plate.

After approximately 5 minutes of production, both the liquid jet source and the sputter source are terminated, the vacuum chamber vented, and the frozen sample allowed to defrost into a glass beaker whilst still under vacuum. The chamber is the returned to atmospheric pressure and the bell jar removed. Liquid samples were then collected, and analysed using UV-Vis spectroscopy. Figure 5 shows the experimental set-up from the point of view of the liquid jet. The sputter head system (represented schematically in figure 2) is pictured in operation, with an intense violet argon plasma glowing above the target. Figure 6 shows a schematic of the production process, adapted from McNally, Galinis, Youle, Chantry and von Haeften (2016) page 3.
Figure 5: Experimental set-up pictured from the point of view of the liquid jet. The solvent micro-jet fires out of the customised HPLC fitting, passes through a vapour of metal atoms generated by the ion sputter source and freezes on the cylindrical glass cold trap.
Figure 6: Schematic of the liquid jet production process, adapted from McNally, Galinis, Youle, von Haeften, and Chantry (2016) page 3. A narrow jet of ethanol is injected into vacuum through a 50 µm capillary (A), which then passes through a vapour of silver atoms evaporated from an argon ion sputter source (B) and freezes on a liquid nitrogen cooled glass cold trap (C). Silver atoms from the sputter source rapidly dissolve in the liquid jet (D), nucleating into small nanoclusters, which are then passivated by the solvent molecules (E) before reaching the cold trap. Once the experiment is terminated, the sample is defrosted into the beaker (F) and collected. The dome shaped umbrella (G) prevents excess silver sputtered onto the S-Bend (H) from collecting in the sample. Liquid nitrogen can be poured into the custom-built bell jar, such that the cold trap can be cooled whilst the apparatus are under vacuum.
3 UV-Vis Spectroscopy

Samples produced in this experiment were analysed using UV-Vis spectroscopy. UV-Vis (Ultra-violet / Visible light) spectroscopy is a powerful analytical tool for a number of reasons. It enables the comparison of many samples with great ease, and can often be used without the need of prior sample knowledge. By comparing the spectroscopic fingerprints of various samples, it is simple to determine if their electronic structures differ. In addition, it is also useful for examining metallic, or potentially metallic, clusters. Typically, a broad absorption band at approximately 400 nm indicates the plasmon resonance of silver nanoparticles (Kreibig and Genzel, 1985; Sau et al., 2010). A plasmon resonance is the resonant oscillation of free electrons at the surface in a material under the influence of a time varying external electronic field, such as electromagnetic waves, and is a strong indicator that the material is metallic. In general, a broad plasmon resonance indicates a broad size distribution of nanoparticles, and furthermore, the absorption intensity of the plasmon resonance decreases with decreasing nanoparticle size (Kreibig and Genzel, 1985). Peng et al., (2010) however, demonstrated that the band position of the plasmon resonance exhibits exceptional size-dependence for silver nanoparticles (coated in OAm, and suspended in hexane). As the particle size decreased from 20 nm to 12 nm, the plasmon resonance gradually blue shifted. This can be attributed to radiative depolarisation effects that occur when the particle size is not comparable to the size of the wavelength (Kelly et al., 2002). As particle size decreased from 12 nm to 2 nm, however, a significant red shift occurred. It was hypothesised this was due to a lowered conductivity in the outer metallic layer due to surface interactions with the chemical surfactant (Peng et al., 2010). The intensity and position of the plasmon resonance, however, can also be influenced by many other factors, including the morphology, composition and surface chemistry of the nanoparticles and the surrounding environment, and as such in this investigation we do not attempt to infer particle sizes from the size and shape of plasmon resonances. Instead, the plasmon resonance was used to assess the nanoparticles’ colloidal stability, since over time, this feature remains consistent in those samples that have remained colloidaly stable (Mcnally, Galinis, Youle, Chantry and von Haeften, 2016). Also present in the UV-Vis spectrum for the
silver nanoparticles produced in this investigation, was an intense absorption at 277 nm. UV-Vis absorption in this region has been recorded for very small silver clusters, \( \text{Ag}_2 \) and \( \text{Ag}_3 \) clusters, frozen in rare gas matrices (Ozin and Huber, 1978; Lecoultre, Rydlo and Félix, 2007) however as shown later, this feature could also related to the presence of solvent molecules. Regardless of this cause of this feature, its evolution was monitored, as an additional method of measuring the colloidal stability of the nanoparticle samples.

Fundamentally, UV-Vis spectroscopy functions by measuring the amount of ultraviolet and visible light that is absorbed by a sample. When the sample is illuminated, photons are absorbed when electrons within the material are excited to higher energy states, producing a spectral feature at the relevant wavelength. The ‘absorbance’ of light at a specific wavelength, \( \alpha_\lambda \), is given as \( \alpha_\lambda = \log_{10}(I_0/I_1) \), where \( I_0 \) is intensity of the incident light, and \( I_1 \) is the intensity of light transmitted through the sample. The table below illustrates how the absorbance, \( \alpha_\lambda \), corresponds to the percentage of light absorbed by a sample.

<table>
<thead>
<tr>
<th>( \alpha_\lambda )</th>
<th>% Absorbed by Sample</th>
<th>( I_1 )</th>
<th>( I_0/I_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0% Absorbed</td>
<td>100% Transmitted</td>
<td>1</td>
</tr>
<tr>
<td>0.25</td>
<td>43.77% Absorbed</td>
<td>56.23% Transmitted</td>
<td>1.778410101</td>
</tr>
<tr>
<td>0.5</td>
<td>68.38% Absorbed</td>
<td>31.62% Transmitted</td>
<td>3.162555345</td>
</tr>
<tr>
<td>1</td>
<td>90% Absorbed</td>
<td>10% Transmitted</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>99% Absorbed</td>
<td>1% Transmitted</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>99.9% Absorbed</td>
<td>0.1% Transmitted</td>
<td>1000</td>
</tr>
<tr>
<td>4</td>
<td>99.99% Absorbed</td>
<td>0.01% Transmitted</td>
<td>10000</td>
</tr>
</tbody>
</table>

**Figure 7:** The absorbance at a specific wavelength, \( \alpha_\lambda \), is the logarithm of \( I_0/I_1 \). Consequently, as seen from the table, the difference between an absorbance of 2 and 4 is barely discernible. In either case, to a good approximation, the sample is opaque at this wavelength.
The main components of a UV-Vis spectrophotometer are a broadband light source (in this instance a xenon flash lamp), a monochromator, a beam splitter (half-silvered mirror), two identical photodiode detectors, and two cuvettes (Suprasil® quartz vessels, path length 10 mm, chamber volume 400 µl, 200 nm – 2,500 nm spectral range). The monochromator filters light from the xenon lamp so that only light of a single wavelength progresses. This light beam is then split into two by a half-silvered mirror. Exactly 50% of the light passes through a reference cuvette and the intensity of the light received is measured by the first photo-diode, whilst the remaining 50% irradiates the sample cuvette before reaching the second photo-diode. The first photo-diode detector is used to measure the intensity of the incident light, $I_0$; the second photo-diode detector is used to measure the intensity of the light that transmits through the sample, $I_1$. In this experiment, the reference cuvette was filled with HPLC-grade ethanol (0.2% water). Hence, when the software (*Thermo Insight*) measures the absorbance at a given wavelength, $\alpha$, it measures only the absorbance of the silver nanoparticles in the sample, or more specifically, what has changed in comparison to the pure HPLC-grade ethanol. The scanning monochromator then moves the diffraction grating to "step-through" increments of wavelength so that a spectrum of wavelength versus absorbance is produced. In this investigation, a Thermo Evolution™ 220 UV-Vis Spectrophotometer was used to record the absorbance spectra. The resolution (bandwidth) of the spectrophotometer was set to 2 nm, and the increment steps set to 1 nm. Integration time was 0.20 seconds per increment step, and the wavelength range was set to iterate from 1000 nm to 200 nm. A baseline measurement was established before the commencement of any measurements using HPLC-grade ethanol in both cuvettes to eliminate any possible background effects. Figure 8 shows a simple schematic explaining the UV-Vis spectroscopy process.
Figure 8: Flow diagram of a UV-Vis spectrometer. A beam of monochromatic light from a xenon flash lamp is split into two by a half-silvered mirror. The intensity of light received by the reference diode is subtracted from that of the sample diode to give only the absorbance of only the nanoparticles present in the sample.
4 IMPROVEMENTS TO THE EXPERIMENTAL SET-UP AND THEIR IMPACT ON SILVER AND WATER CONCENTRATION

In this project, a number of modifications were made to the experimental set-up in order to improve the control one has over the quantity of silver and water present in each sample. Nevertheless, a certain degree of uncertainty still remained over the reliability of some samples that were produced, due to the difficulty in keeping a liquid jet stable in a vacuum environment. Consequently, out of twenty samples produced, eight were selected for further analysis. The results of which are presented in section 7. This section summarises the key modifications made in order to improve experimental reliability. It should be stated that all samples produced in this investigation were done so via the jet co-deposition (JCD) mechanism.

4.1 Improving the Purity using the New Experimental Set-up

The first, and possibly, most important modification to the experimental set-up was the development and inclusion of the new glass cold trap, which can be filled with liquid nitrogen whilst the chamber is under vacuum (see figures 1, 5 and 6). This ensures water vapour from the air cannot condense on the cold trap, and thus reduces the water concentration in the samples by an order of magnitude, as shown below.

In previous investigations, one was first required to cool a stainless steel cold trap in a bath of liquid nitrogen and then transfer the cold trap through air to the vacuum chamber; consequently, water in the air condensed on the cold trap, forming ice crystals.
The original cylindrical stainless steel cold trap (figure 9) had dimensions of 41 mm inner diameter, 48 mm outer diameter and a height of 140 mm. The cold trap also had a window of 30 mm by 40 mm through which the liquid jet entered. The foil covering the stainless steel cold trap, which also wrapped around the petri dish that the sample defrosted into, was put in place to help exclude water vapour from condensing on the cold steel surface. Despite taking this preventative measure, frozen water vapour on both the inner surface, and the outer surface beneath the foil were still observed.

![Figure 9: The stainless steel cold trap used in previous investigations needed to be cooled first and then transferred to the vacuum chamber. Consequently, water vapour condensed on the surface, contaminating the samples (Youle and von Haeften 2015). Pictured on the left is the cold trap in action, with solvent freezing on the interior wall. On the right, is the cold trap drawn schematically, with a foil wrapping which encased both the cold trap and the petri dish. The purpose of the foil casing was to restrict water vapour from condensing on the steel surface and later defrosting into the sample.]

To measure the volume of water that collected in the petri dish from water vapour condensing and freezing on the cold trap, one simply allowed the frozen crystals to defrost. Using a micro-pipette it was shown that 0.55 ± 1.8 ml of water resulted, contaminating the samples. When production was run for five minutes the approximate volume of sample produced was 10 ml. Therefore, all previous samples have water contamination in the order of 6%:
In order to identify the potential impact that water contamination had on the liquid jet samples the new cold trap arrangement was introduced to eliminate the opportunity for water from the air to condense on the cold trap. In the amended set-up, the only source of water in the pure samples produced in this investigation was from that originally dissolved in the HPLC grade ethanol; HPLC ethanol has a purity of 99.5% and contains 0.2% water, and as such in a 10 ml sample, only 0.02 ml of water was present. Therefore, by replacing the stainless steel cold trap with one that can be cooled under vacuum, the purity was improved by an order of magnitude:

\[
\frac{0.55 \pm 0.18 \text{ ml}_{\text{water}}}{0.02 \text{ ml}_{\text{water}}} = 27.5 \pm 9
\]

Of course, there is a certain solubility of water in ethanol, which could have condensed from air whilst setting up the experiment. Nevertheless, it was ensured that the time that the ethanol was exposed to air was minimised, and so this source of contamination is considered to be negligible.

With water vapour eliminated from condensing on the cold trap, the water concentration could be purposefully varied by pippeting solutions of specific concentrations into the liquid jet reservoir. The different concentrations used in this investigation, which were pipetted into the liquid-jet chamber, were: 10% water, 90% HPLC grade ethanol; 1% water, 99% HPLC grade ethanol, and pure HPLC grade ethanol (which included 0.2% water).

**4.2 Controlling Silver Concentration**

A number of improvements were also made which allowed a better understanding of the concentration of silver that resulted in the samples. Despite already producing some very exciting results, the liquid jet technique can still be considered in its prototype stage. As such, the silver concentration depends very much on the instantaneous conditions in the vacuum chamber. By paying close attention to these instantaneous conditions, it was possible to better control the silver concentration, and also improve the productivity of our technique.
4.2.1 The Trajectory of the Liquid Jet Directly Affects Silver Concentration

In this investigation, close attention was paid to the trajectory of the liquid jet. It was observed that on many occasions the jet would behave unpredictably, and drift, bend, and occasionally miss the cold trap. Fundamentally, this occurred because a liquid was introduced to a vacuum. Liquids and vacuums do not typically co-exist. By their very nature, liquids evaporate and hence spoil the vacuum. In this set-up however, the liquid jet rapidly froze on the cold trap, thus allowing, at least for a short while both a metastable liquid template and a vacuum to co-exist. It was observed however, that when the trajectory of the liquid jet did bend, and miss the cold trap, the sputter source would temporarily cease because the pressure in the chamber had increased; it can only operate under vacuum conditions. Consequently, for samples where the jet did not consistently strike the cold trap, one can be confident the samples contained less silver. Samples EX14-Low_Ag-1%_H2O, EX15-Low_Ag_10%_H2O, EX16-Low_Ag-10%_H2O and EX17-Low_Ag-10%_H2O, presented in figure 15 in section 7, results and discussion, are good examples of this.

In an attempt to understand why the liquid jet’s trajectory would bend, a number of hypotheses were tested. Firstly, it was hypothesised that the jet may be electrically charging. Electrons could be stripped from the liquid molecules via friction in the silica capillary, resulting in the jet being repelled or attracted by the plasma, or charged surfaces. Attaching electrodes and applying a potential to the capillary, however, yielded no evidence to support this theory.

Secondly, it was observed that there was potential for the solvent to freeze at the end of the capillary due to the low pressure. This could cause a blockage that could physically deflect the jet, and would be especially prevalent if water was introduced into the solvent reservoir (since water has a higher freezing point than solvents such as ethanol). To counter the possibility of freezing solvent, a custom-built light-bulb heater was introduced to gently heat the solvent and melt any blockages (as labelled in figure 5). The light bulb would heat the capillary via radiation. In previous investigations, attempts had been made to test this hypothesis. The radiative energy, however, decays according to the relationship $\frac{1}{r^2}$, where r is the radial distance from the centre of the light bulb, and as such, it was difficult to supply heat to the capillary. To increase the amount of energy supplied to the capillary in this investigation, an aluminium sheet was folded around the indicator light bulb and around the perimeter of the capillary. Since the
aluminium sheet is heated via conduction, the radial distance was reduced, whilst also allowing the capillary to be heated from all sides, see figure 10. Unfortunately, it was not conclusive as to whether heating the jet had a noteworthy effect on its trajectory. Nevertheless, the new light-bulb configuration was useful in illuminating the jet (so one could see its exact trajectory) as well as physically protecting the capillary from atomic silver depositing upon it, and hence the addition was kept in place.

![Figure 10](image)

Figure 10: To increase the amount of heat supplied to the capillary, an aluminium sheet was folded around the circumference the indicator light bulb, and the capillary, as shown on the right. This reduced the radial distance from which heat would radiate, and allowed the capillary to be heated from all sides. On occasions, the aluminium sheet would also rest against the capillary, allowing the heat to conduct as well as radiate. This custom-built heater mounted to HPLC fitting holding the capillary, and can be seen in figure 5.

Thirdly, in previous investigations (Youle and von Haeften, 2015) efforts were made to replace the solvent in the solvent reservoir after each experiment. The reasoning behind this was that it had been observed that argon gas, used to force the solvent out of the capillary, was dissolving in the solvent; the solvent contained many numerous microscopic bubbles post-production. It was hypothesised that these argon bubbles might be responsible for the blockages that could explain the random trajectories of the jet. To address this possibility, in the current investigation the solvent reservoir was emptied after every experiment; and between experiments, the customised reservoir was disassembled and each component, including the HPLC fitting was re-mounted in turn to the BOC Edwards argon cylinder. Argon was forced through the components, flushing out any
solvent residue to ensure the assembly was clean for the next experiment. Whilst such practice did not completely stop the liquid jet’s trajectory from drifting, a considerable improvement was noted.

Although it was not conclusive exactly which modification had the greatest impact upon the liquid jet, together the adaptations improved the stability of the system and increased the productivity of the liquid jet technique by over 300%. Before such modifications, one could produce at most one sample per day, afterwards it became possible to produce at least three samples per day; an improvement that will prove highly desirable to future practical applications for this system. Despite this however, the instantaneous conditions in the vacuum chamber still represented the biggest cause of fluctuations in silver concentration that resulted in the samples. Nevertheless, for this investigation, the observations of whether the jet behaved consistently, allowed us to determine whether the sample would have a comparatively low or high concentration of silver.

4.2.2 Umbrella Shield Assists in Controlling Silver Concentration

Another modification, which has not yet been addressed, was the inclusion of the umbrella shield. Using the new set-up, whereby one could pour liquid nitrogen into the cold trap whilst the chamber was under vacuum, a new source of error was inadvertently caused; silver could also deposit onto the S-bend which joined the liquid nitrogen inlet to the cold trap. Due to the geometry of the set-up, the concentration of silver on this surface area was much higher. Consequently, when the cold trap and connecting S-bend defrosted, this excess silver would collect in the sample. Although this excess still contained sputtered silver atoms that mixed with ethanol, it was feared such a large concentration of silver would

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure11.png}
\caption{Schematic of the customised glass dome sealed to the cylindrical glass cold trap. Large quantities of silver deposited onto the S-Bend due to the geometry of the sputter source. To prevent such large quantities of excess silver from contaminating the sample, a dome shaped aluminium umbrella was installed.}
\end{figure}
overshadow other effects, such as varying the water content. Further, it was not possible to keep the quantity of excess silver that was deposited in the sample in this manner constant. As such, an aluminium umbrella-shaped shield (seen in figure 11) was manufactured to exclude the excess silver from forming part of the sample. Once this shield was in place, no further deposits of silver from the S-bend resulted in the sample. Sample EX7-High_Ag-1%_H2O was produced before the inclusion of the umbrella shield. Consequently, due to the additional silver that deposited on the S-bend, which also formed part of the final sample, the concentration of silver in this sample was approximately twice that usually expected.

4.3 Estimating Silver and Water Concentration

Using modifications such as the cold trap to reduce water content, and the umbrella shield to restrict excess silver from forming part of the sample, and by paying particular attention to the behaviour of the liquid jet, which directly affects the silver concentration; it was possible to estimate the silver and water concentration that resulted in the new samples produced. First, silver concentration is considered:

Assuming the sputter head was a point source, a vapour of metal atoms were emitted radially in all directions. Consequently, the measured deposition rate falls as a function of \( r^2 \), as the linear distance, \( r \), away from the point source increased. This is because the total flux of atoms remains constant. For all the samples produced in this project, the sputter current was kept constant at 0.20 A and the chamber pressure at \( 1 \times 10^{-2} \) mbar. Therefore, using a deposition rate of 3.4 \( \text{nm min}^{-1} \) as measured by the XTM (at a distance 30 cm from the sputter source, see figure 1) the deposition rate at the position of the liquid jet (and at the cold trap) is:

\[
\text{deposition rate at jet} = \text{deposition rate at XTM} \times \left( \frac{\text{XTM distance}}{\text{jet distance}} \right)^2.
\]

The radial distance from the sputter target to the liquid jet stream (and the cold trap), was approximately 6 cm. Therefore, the deposition rate of silver at the jet and cold trap position was approximately 86 nm \( \text{min}^{-1} \):

\[
\text{deposition rate at jet} = 3.4 \text{ nm min}^{-1} \times \left( \frac{30 \text{ cm}}{6 \text{ cm}} \right)^2 = 85.625 \text{ nm min}^{-1}.
\]
To calculate the volume of silver that should result in the samples, this deposition rate was multiplied to the area to which it deposits on; i.e. for JCD samples, the liquid jet and the cold trap. The area of the jet was approximately $1.5 \times 10^{-4}$ m$^2$, and the area of the cold trap equalled $4 \times 10^{-4}$ m$^2$. Calculations for such areas are shown in appendix 3. As such, the volume of silver that formed part of the samples was:

$$\text{volume of silver in sample (per unit time)} = (\text{area of jet} \times \text{deposition rate}) + (\text{area of cold trap} \times \text{deposition rate})$$

$$= 4.73 \times 10^{-11} \text{ m}^3 \text{ (per unit time)}.$$

The density of silver is 10490 kg m$^{-3}$. Consequently, 0.496 mg of silver was deposited into the sample per unit time. The molar mass of silver is 107.8682 g mol$^{-1}$. Hence, $4.6 \times 10^{-6}$ moles of silver were deposited into sample per unit time. This equates to $2.77 \times 10^{18}$ silver atoms, per unit time. Considering each experiment ran for approximately 5 minutes, and provided production ran consistently throughout the experiment, each sample contained approximately $1.39 \times 10^{19}$ silver atoms.

The largest source of error in this estimate, comes from estimating the area to which the silver deposits. In addition, not 100% of the silver that deposits onto the liquid jet would be trapped by the solvent molecules and form part of the sample. Consequently, the error in this calculation is estimated to be ± 25%. Of course, as previously mentioned, the concentration of silver that resulted in the samples depends largely on the instantaneous conditions in the chamber. For example, for samples where the liquid jet missed the cold trap, causing the sputter source to turn off, approximately half the concentration of silver can be expected. This was because the sputter source only sputtered for approximately 50% of the time. Nevertheless, this calculation gives us a good approximation of the quantity of silver that results in the samples.

Next, the quantity of water in the samples was considered. A typical sample was 10 ml in volume. Hence, the ‘pure’ samples contain 0.02 ml of water. This contribution of water was that originally dissolved in the HPLC-grade ethanol. Since water has a density of 1 g ml$^{-1}$, and a molar mass of 180.15 g mol$^{-1}$, there were approximately 0.00011
An Investigation Into The Colloidal Stability Of Silver Nanoparticles Produced In Ethanol Micro-Jets

moles of water are present in such samples. This equates to $6.68 \times 10^{19}$ molecules of water.

Consequently, one can conclude, that for the samples produced via the liquid jet technique in this investigation, the number of water molecules exceeds the number of silver molecules. For HPLC grade ethanol only samples, the ratio of silver atoms to water molecules was approximately 0.2: 1.

\[
\frac{\text{Silver Atoms}}{\text{Water Molecules}} = \frac{1.39 \times 10^{19}}{6.68 \times 10^{19}} = 0.2
\]

In fact, the number of water molecules even exceeds the number of silver atoms for even the highest silver concentration sample produced in this investigation; sample EX7-High_Ag-1_%_H2O contains approximately twice that of typical samples. Sample EX7 contains approximately twice the concentration of silver of typical samples because it had an additional surface area (the S-Bend) of approximately $5 \times 10^{-4}$ m$^2$, to which silver deposited on. To completely eliminate the contribution of water, a drying agent could have been used. Time limitations prevented pursuit of this line of investigation in the current study, however, this remains an option for future investigations. In this investigation, although water is not eliminated completely, since the relative concentrations of silver and water were known, the water content was purposefully varied to investigate its effect on the colloidal stability and nanoparticle formation.
Figure 12 shows an example UV-Vis spectrum for a sample of silver nanoparticles produced in ethanol at $t = 0$ minutes and $t = 4$ days. As described in section 3, the spectrum of ethanol has already been subtracted from the spectrum presented in figure 12 because the spectrometer has been set up, in this instance, to use HPLC-grade ethanol as a reference, and hence the spectral features presented only result from absorption due to nanoparticles. For the interpretation of the data however, one also needs to consider the interaction silver has with ethanol, and the interaction silver has with water, and all cross interactions, because as shown in section 4, the number of water molecules exceeds the number of silver atoms in all of the samples.

Figure 12: Example UV-Vis spectra of a silver nanoparticle sample produced in ethanol at $t = 0$ minutes and $t = 4$ days, illustrating three distinct features at 240 nm, 277 nm and a broad feature at 480 nm (the plasmon resonance.)
In figure 12, three distinct features can be observed. The first feature is a plasmon resonance, which for \( t = 0 \) minutes, occurs at approximately 480 nm. Such a feature is consistent with the presence of metallic nanoparticles in ethanol (Kreibig and Genzel 1985). At \( t = 4 \) days, the plasmon resonance red-shifted, and peaked at approximately 560 nm, as well as apparently increasing in absorbance and broadening.

The second important feature, centred at approximately 277 nm, is only present in the \( t = 4 \) days measurement, but is consistent in all nanoparticle samples produced by the liquid jet technique. It is possible that very small nanoparticles, similar to \( \text{Ag}_2 \) or \( \text{Ag}_3 \) may be responsible for this peak (which is referred to as the ‘shoulder’) because similar peaks have been seen in literature (Ozin and Huber, 1978; Lecoultre, Rydlo and Êlix, 2007). Hydroxide compounds, for example AgOH, could also be a possible contributor for this peak however. This is because, as shown, water is in excess of silver for all of our samples, so stands to reason hydroxide compounds could be present. Although it was not possible to specifically determine what particles or process may be responsible for the appearance of the second spectral feature at first glance, its evolution was monitored regardless because it was evident something was changing over time, since it was not present at \( t = 0 \) minutes, and at this stage of investigation it was overall stability that is of concern; it would be an interesting line of future investigation to identify the exact origin of the shoulder feature.

The third feature is the peak centred at 240 nm, which has an absorbance of approximately 1.6 for both the \( t = 0 \) minutes measurement and the \( t = 4 \) days measurement. An absorbance of 1.6 tells us that approximately 97.5% of the incident light was absorbed by the sample (refer to figure 7). Consequently, whatever is responsible for this peak is to good approximation opaque at this wavelength. Unfortunately, one cannot be certain that this peak does not change over time, because even in the first measurement, the vast majority of light was absorbed. It would potentially be possible to investigate this peak using a range of dilute the samples, however, time constraints and sample availability prevented investigation of this during this current investigation; nevertheless, it is later shown that hydroxyl ions may be responsible for this peak.

Referring back to the \( t = 0 \) minutes measurement in figure 12, it is possible to identify two distinct components in the spectrum: a Gaussian shaped plasmon resonance, superimposed on another first component, which includes the 240 nm peak.
Consequently, to measure the peak absorbance of the plasmon resonance, it seems sensible to subtract the first component. The following section explains how this is done, and thereafter the method is justified.

To subtract the first component, one graphically interpolates the trajectory of the first component (i.e. one graphically sketches out the curvature of the first component between 300 nm and 900 nm). The graphical interpolation is an estimate, and hence could be subjective, but it was drawn such that the interpolation is a smooth and consistent decay. In doing this it was also assumed this ‘first component’ was not variable. Then, the peak plasmon absorbance was taken to be the difference between the maximum absorbance of the Gaussian shaped plasmon resonance and the interpolated absorbance of first component at the same wavelength (see figure 13). Due to the ambiguity involved in estimating the first component, the error in the peak plasmon resonance absorbance is taken to be plus or minus one grid bar, as the curve could also be feasibly drawn at these trajectories. For the spectra in figure 13, this is ± 0.02.

**Figure 13:** To find the maximum absorbance of the spectra’s plasmon resonance, the absorbance from the first component is subtracted. The first component’s trajectory is estimated, shown in red for t = 0 minutes and violet for t = 4 days. The error in the plasmon resonance absorbance is ± 0.02.
In many metallic samples produced by the liquid jet, a plasmon resonance is observed. Over time however, for certain samples, as shown later, this plasmon resonance disappears. For silicon samples produced in ethanol using the liquid jet, a similar absorbance spectrum is observed; however, such spectra do not contain a plasmon resonance because the particles are not metallic (Uwuigbe and von Haeften, 2016). Additionally, for low silver concentration samples the plasmon is comparatively weak; again, as shown later. Consequently, there is a large amount of reference material of spectra without a plasmon resonance. Using these references, it is possible to visualise the spectra as two separate components, and hence one can justify making this graphical interpolation and subtraction. Furthermore, figure 14 below, shows how the plasmon resonance absorbance changed over time for the example silver in ethanol sample pictured in figure 12 and 13. As can be seen from figure 14, if the ‘first component’ was not subtracted, and one simply took the absorbance to be the peak of the plasmon resonance as measured from zero (red data points) the data set fluctuated, rather than followed a trend. In comparison, if the ‘first component’ was subtracted via the graphical interpolation method as described above, the data set appeared to follow a trend (black data points). This result was typical of every sample analysed. Consequently, it was considered that the graphical subtraction method, although based upon an estimation, was reliable.
Figure 14: Peak plasmon resonance absorbance of example silver nanoparticle sample shown in figure 12 over time. Shown in black is the peak absorbance of the plasmon resonance as measured via graphical subtraction of the first component. Shown in red is the peak absorbance of the plasmon resonance as measured from zero.

Using regression analysis to fit a curve to the graphical interpolation data set (black data points), it was revealed that data follows exponential decay with two terms, and two time constants. This suggests two processes were occurring, providing further reasoning to trust the graphical interpolation method; because a curve can actually be fitted. In comparison a curve cannot be fit to the red data set, where the peak absorbance was measured from zero. Note that the time constants for all curves are given in minutes.

Because the graphical subtraction method yielded a more consistent trend in how the plasmon resonance intensity changed over time, rather than a data set that fluctuated, this method was adopted to measure the plasmon resonance intensities of all the samples in this investigation. By monitoring the peak absorbance intensities and peak wavelengths of features such as the plasmon resonance and the shoulder, and their evolution over time, samples were compared to infer certain physical characteristics. Specifically, the evolution of such peaks was monitored to assess the colloidal stability of the nanoparticles.
6 RESULTS AND DISCUSSION

The primary goal of this project was to assess how the concentration of water present in the samples affected the colloidal stability of the silver nanoparticles produced. To achieve this goal, a set of twenty samples were produced under various conditions. Eight of which were selected, based upon their reliability and our confidence over experimental control, for further analysis. Variables altered were the concentration of water and the concentration of silver. Upon production, coloured samples (usually pink) were obtained, which yielded a plasmon resonance in the UV-Vis spectra between 400 nm and 700 nm. By measuring observables in the UV-Vis spectra, such as the absorbance intensity of the plasmon resonance, and of other features (at 240 nm and 277 nm) and by measuring their wavelength, and how the intensity and wavelength changed over time, it was possible to assess how the variables affected colloidal stability and nanoparticle formation. A summary of the samples investigated is presented in figure 15. Full results and analysis are presented thereafter.

Figure 15 shows a summary of the samples investigated in this project. The silver concentrations of the samples are based upon the deposition rate and the surface area to which the silver deposits, as calculated in section 4.3. An error of 25% is estimated for such calculations. Samples EX14, EX15, EX16, and EX17 have a low concentration of silver, because the sputter source turned off intermittently. It is estimated they contain approximately half the silver concentration that might be expected, because the sputter source was only operational for approximately half of the production time. Sample EX7 has approximately twice the quantity of silver of EX9, because silver that also sputtered onto the S-bend was allowed to result in the sample; this more than doubles the surface area to which silver can sputter on. The water concentration was varied purposefully by pipetting known amounts of water into ultra-pure ethanol. The number of water molecules this corresponds to is calculated in section 4.3.
### Figure 15:
A summary of the eight samples investigated in this project.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Silver Concentration (atoms)</th>
<th>Water to Ethanol Ratio</th>
<th>Water Concentration (molecules)</th>
<th>Silver to Water Ratio (Ag atoms : H₂O molecules)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EX7</td>
<td>$2.78 \times 10^{19}$ ± $0.70 \times 10^{19}$</td>
<td>1% Water, 99% Ethanol</td>
<td>$3.34 \times 10^{20}$</td>
<td>~ 0.08 : 1</td>
</tr>
<tr>
<td>EX9</td>
<td>$1.39 \times 10^{19}$ ± $0.35 \times 10^{19}$</td>
<td>0.2% Water, 99.8% Ethanol</td>
<td>$6.68 \times 10^{19}$</td>
<td>~ 0.2 : 1</td>
</tr>
<tr>
<td>EX10</td>
<td>$1.39 \times 10^{19}$ ± $0.35 \times 10^{19}$</td>
<td>10% Water, 90% Ethanol</td>
<td>$3.34 \times 10^{21}$</td>
<td>~ 0.04 : 1</td>
</tr>
<tr>
<td>EX13</td>
<td>$1.39 \times 10^{19}$ ± $0.35 \times 10^{19}$</td>
<td>0.2% Water, 99.8% Ethanol</td>
<td>$6.68 \times 10^{19}$</td>
<td>~ 0.2 : 1</td>
</tr>
<tr>
<td>EX14</td>
<td>$6.9 \times 10^{18}$ ± $1.73 \times 10^{18}$</td>
<td>1% Water, 99% Ethanol</td>
<td>$3.34 \times 10^{20}$</td>
<td>~ 0.02 : 1</td>
</tr>
<tr>
<td>EX15</td>
<td>$6.9 \times 10^{18}$ ± $1.73 \times 10^{18}$</td>
<td>10% Water, 90% Ethanol</td>
<td>$3.34 \times 10^{21}$</td>
<td>~ 0.002 : 1</td>
</tr>
<tr>
<td>EX16</td>
<td>$6.9 \times 10^{18}$ ± $1.73 \times 10^{18}$</td>
<td>10% Water, 90% Ethanol</td>
<td>$3.34 \times 10^{21}$</td>
<td>~ 0.002 : 1</td>
</tr>
<tr>
<td>EX17</td>
<td>$6.9 \times 10^{18}$ ± $1.73 \times 10^{18}$</td>
<td>10% Water, 90% Ethanol</td>
<td>$3.34 \times 10^{21}$</td>
<td>~ 0.002 : 1</td>
</tr>
</tbody>
</table>
6.1 Silver Nanoparticles in Ultra-Pure Ethanol

The results presented in this sub-section are related to samples that were produced using pure HPLC-grade ethanol, and thus contain 0.2% water (samples EX9-High_Ag-0.2%_H$_2$O and EX13-High_Ag-0.2%_H$_2$O; see figure 15 above). Such samples contain the lowest concentration of water ever produced via the liquid jet. Upon production, coloured samples (usually pink) and a surface plasmon resonance in the 400 nm to 700 nm region were observed, which implies that the sample contains metallic nanoparticles (Kreibig and Genzel 1985). With all samples produced by the liquid jet technique the colour fades over time; those that appeared golden brown initially transitioned to pink and then finally to clear, and those that were produced pink, faded from pink to clear. It was also noted that as the samples faded to clear, black macroscopic agglomerates precipitated out of solution. The black macroscopic agglomerates are denser than the solution, and hence settle at the bottom of the sample vial. It is hypothesised the observed colour transition is consistent with nanoparticles in the sample aggregating over time. The rate of this aggregation, however, varied from sample to sample, taking between 10 minutes, and several hours.

Figure 16 shows photographs of sample EX9-High_Ag-0.2%_H$_2$O taken immediately after production, at the time of the first UV-Vis measurement ($t = 0$ minutes) and at the time of the second UV-Vis measurement ($t = 5$ minutes). Figure 17 shows the respective UV-Vis measurements for sample EX9-High_Ag-0.2%_H$_2$O as it evolves over time. Figure 18 shows the evolution of the UV-Vis spectra of sample EX13-High_Ag-0.2%_H$_2$O; a second silver in pure ethanol sample, which also contains 0.2% water.
Figure 17: UV-Vis Spectra of EX9-High_Ag-0.2%_H$_2$O, silver nanoparticles produced in ethanol with 0.2% water. Initially, the nanoparticles are metallic – as deduced from the plasmon resonance – however, after a period of 10 minutes an instantaneous reaction occurs and the plasmon resonance spectra vanishes. In this experiment, the sample was exposed to light, and also shaken before each UV-Vis measurement was taken so as to homogenise the sample.
As shown in figure 16, a rapid colour change occurred in sample EX9-High_Ag-0.2%_H$_2$O; in a matter of minutes after production, the visual appearance of the sample changed from gold (before the first UV-Vis measurement is taken) to red/deep pink (at the time of the first UV-Vis measurement) to clear as black agglomerates precipitated out of solution (at the time of the second UV-Vis measurement, $t = 5$ minutes). Despite this colour change, between UV-Vis measurements, the plasmon resonance, as apparent in figure 17, is relatively consistent over the same time interval. This suggests the colour change is independent of the plasmon resonance. In fact, it could be the sources of underlying spectral features in the spectrum which affect the transmission of light much more distinctly than the source of the plasmon resonance. Regardless, the presence of the plasmon resonance suggests that the sample contains metallic nanoparticles; hence, it can be inferred that, despite the colour change, and precipitation, metallic nanoparticles remain present throughout this initial period of observation.

Subsequent to the $t = 5$ minutes measurement the sample did not drastically alter in appearance (although agglomerates continued to grow), however, in the UV-Vis spectra a noticeable change occurs. The plasmon resonance suddenly disappears after a period of 10 minutes, indicating that an avalanche-type reaction must have occurred causing the nanoparticles responsible for the plasmon resonance to disappear or change.
Figure 18: UV-Vis Spectra of EX13-High_Ag-0.2%_H₂O; a second, separate sample of silver nanoparticles produced in ethanol with 0.2% water.

For sample EX13-High_Ag-0.2%_H₂O, also silver nanoparticles produced in pure HPLC-grade ethanol (0.2% water), similar observations were made. On production, the sample was a prominent pink colour. The colour of the sample began to fade immediately, and within an hour the pink colour had completely faded, and black agglomerates had settled out. In the UV-Vis spectra, shown in figure 18, a plasmon resonance of slightly higher intensity to that of sample EX9-High_Ag-0.2%_H₂O was observed, which diminished significantly in intensity at the $t = 30$ minute UV-Vis measurement. For this sample, in contrast to sample EX9, it appears the time frame of the plasmon resonance decay correlates with the rate of colour change. Nevertheless, the plasmon disappears in a similarly sudden fashion suggesting an instantaneous avalanche type reaction has occurred.

One possible explanation for this difference in reaction speed is the quantity of silver present in solution. In the following section, evidence suggests sample EX13 contains a higher concentration of silver in comparison to sample EX9. Hence, it could be that a higher concentration of silver results in slower agglomeration. Unfortunately, it
An Investigation Into The Colloidal Stability Of Silver Nanoparticles Produced In Ethanol Micro-Jets

is not possible to accurately quantify this concentration of silver. Regardless of the time frames, for both 0.2% water samples, the plasmon resonance completely disappeared, thus, one can conclude, that silver nanoparticles produced in pure ethanol (0.2% water) via the liquid jet technique, are not colloidally stable.

6.2 Silver Concentration affects Plasmon Resonance Intensity

The unpredictable behaviour of the liquid jet trajectory was exploited to produce samples with varying silver concentration. Sample EX17-Low_Ag-10%_H2O in particular, and samples EX14-Low_Ag-1%_H2O, EX15-Low_Ag-10%_H2O and EX16-Low_Ag-10%_H2O are good examples of where the liquid jet missed the cold trap, and despite no quantitative measurements, we are confident they contain a low concentration of silver in comparison to sample EX9-High_Ag-0.2%_H2O, which ran reliably, and consistently for the full 5 minutes of production. For longer production times the effect of a consistent sputter source becomes significant; as the sputter source heats up over time and hence larger quantities of silver are sputtered (Youle and von Haeften, 2014). Hence, the longer the production time, the higher the ratio of silver to ethanol. Sample EX10-High_Ag-10%_H2O is a good example of this as it had a production time of approximately 10 minutes, and thus contained a comparatively high concentration of silver. Sample EX7-High_Ag-1%_H2O has approximately twice the quantity of silver of EX9-High_Ag-0.2%_H2O, because silver that also sputtered onto the S-bend was allowed to result in the sample; this almost doubles the surface area to which silver can sputter on. A summary of the estimated concentrations of the silver present in the samples in this investigation is presented in figure 15, where, for the purposes of this investigation, the samples are categorised into high silver concentration, and low silver concentration. Figure 19 shows the UV-Vis spectra of the eight samples taken at $t = 0$ minutes. From this figure it can be concluded, to a high degree of certainty, consistent with our expectations given the origin of plasmon resonance, the higher concentration of silver, the more intense the peak plasmon resonance intensity. It is noted that the concentration of water varies between these samples. Whilst the presence of water is acknowledged, there appears to be no correlation between water content and initial plasmon resonance intensity, indicating this is not a relevant factor in these results.
Figure 19: UV-Vis spectra of the eight silver samples produced in ethanol at $t = 0$ minutes. The plasmon resonance intensity depends on the concentration of silver; a higher silver concentration results in a stronger plasmon resonance.

### 6.3 UV-Vis Spectra are Dependent on the Pipetting Process.

As shown in section 6.1, figure 16, over time, the colour of sample EX9-High_Ag-0.2\%H\textsubscript{2}O faded and transitioned from golden brown, to pink, to clear as black macroscopic agglomerates. Such a colour transition was true of all samples. Most samples, however, were produced pink, but nevertheless all still transitioned to clear with agglomerates. To investigate the possible impact that the precipitation of agglomerates may have on the plasmonic response of the samples an experiment was performed pipetting different sections and acquiring their different spectroscopic fingerprints.

In figure 20, three different UV-Vis spectra for sample EX17-Low_Ag-10\%H\textsubscript{2}O are presented after the sample had been allowed to age for 11 days. At this point the sample had fully settled out into a clear solution and dense black macroscopic agglomerates. To record a UV-Vis spectrum, a portion of the sample needs to be pipetted...
into the Suprasil® Cuvette. The three spectra represent three different methods of pipetting the sample.

**Figure 20:** Three UV-Vis spectra of sample EX17-Low_Ag-10%_H₂O, recorded after 11 days, using three different pipetting techniques. When pipetting just the top layer of the solution into the Suprasil® cuvette (blue line) one avoids collecting the dense black agglomerates. The inset shows the absorption in the 400 nm to 800 nm region.

As can be seen from figure 20, the different methods of pipetting the sample resulted in noticeably different UV-Vis spectra. In fact, the absorbance varied by as much as 10% at 277 nm. Such a variation would typically overshadow the effects of the investigation and as such this figure shows that it is crucial the pipetting method was performed consistently.

The first method of pipetting, was to allow the sample to settle (for several hours) and then to pipette only the top layer, as to avoid collecting any of the dense black agglomerates (blue line). As can be seen, this method yielded the weakest absorption in the 400 nm to 800 nm range; it produced no plasmon resonance (shown inset, figure 17) however a considerable absorption 277 nm and 240 nm was still observed. Such a result is interesting. Firstly, the absence of a plasmon resonance in the 400 nm to 800 nm range
indicated there were no metallic particles present in this ‘clear’ solution. Secondly, whatever is responsible for the peak at 277 nm, must have been present in the ‘clear’ solution. The same conclusion can be drawn for the 240 nm peak: the particles causing the absorption were also present in the ‘clear’ solution.

In comparison, if the sample was allowed to settle and then bottom layer of the sample was pipetted, collecting as many dense agglomerates as possible, a noticeable plasmon resonance absorption was observed (red line). Consequently, it is possible that the macroscopic agglomerates themselves could be the source of the plasmon resonance. Alternatively, it is also possible the agglomerates are a collection of plasmonic nanoparticles. If the vial was shaken however, as to break the agglomerates up into microscopic constituents redispersing them to form a homogenous mixture, and this homogenous mixture was sampled, the plasmon resonance maintained a very similar shape (green line). One would expect that the plasmon resonance to change significantly if either of these explanations were true. Hence, it is most likely that source of the plasmon resonance were dense nanoparticles that rest amongst the agglomerates at the bottom of the sample vial.

With regards to the absorbance intensity at 277 nm, the ‘bottom layer’ measurement yielded a stronger absorbance than the ‘top layer’ measurement. Consequently, the particles responsible for this absorbance peak, must have a higher density than ethanol. Candidates for such particles, could be ‘tiny’ Ag₂/Ag₃ nanoparticles. Such particles would have a higher density than ethanol, and similar absorbance spectra for such particles have been reported in literature (Ozin and Huber 1978). Of course, the presence of water in these samples cannot be ignored. The number of water molecules still exceeds the number of silver atoms for all of the samples, as shown in section 5.2. Furthermore, the same ‘shoulder’ feature at 277 nm occurred in every sample produced by the liquid jet technique thus far. A similar result was also observed for silicon nanoparticles produced by the liquid jet (figure 34, Uwuigbe & von Haeften, 2016). Consequently, this suggests this peak is not specific to silver. Previous work conducted by Uwuigbe and von Haeften (2016) suggest nanoparticles produced by the liquid jet undergo a form of hydrolysis reaction. Hence in this instance, the responsible particles could be silver hydroxide compounds, AgOH. To confirm this however, further work would need to be conducted, possibly using infrared spectroscopy to support a more detailed interpretation of UV-vis results.
With regards to the absorbance peak at 240 nm, a similar conclusion can be drawn. Here, the ‘top layer’ measurement yielded a stronger absorbance, than the ‘bottom layer’ measurement. Consequently, the responsible particles must have a lower density than ethanol. It is very unlikely metallic particles are responsible for this absorbance, because they would have a higher density than ethanol. Hence, a strong candidate for this peak could be OH\(^-\) ions. To investigate this further, it would be useful to vary the content of water and then monitor the evolution of this peak. Unfortunately, however, as previously discussed, it would be unreliable to compare the absorbance intensities between spectra, because almost all of the light is already absorbed. One would need to dilute the samples to investigate this further. This is an opportunity for future investigations.

As a result of this experiment, it was decided to shake, homogenise, and redisperse the agglomerates in the samples prior to every measurement. Not only does this method give us the best opportunity to keep the measurements fair and consistent it also allows us to investigate the plasmon response of the nanoparticles. All following figures, unless otherwise stated, represent ‘shaken, homogenous’ samples.

6.4 Adding water increases the colloidal stability of the nanoparticles

The new experimental set-up employed in this investigation allowed the addition of water to the samples in a controlled manner. To produce samples containing more water, a solution of 90% ethanol and 10% water was pipetted into the reservoir. Silver atoms were then sputtered onto the ethanol-water solution, and consequently a controlled amount of water was present in each sample; sample EX10-High_Ag-10\%_H\(_2\)O is one such sample made via this method. The following sections demonstrate how adding water modifies the stability of the resultant nanoparticles.

6.4.1 Comparing Sample EX10 (High Silver, 10% Water) to Sample EX13 (High Silver, 0.2% Water)

Figure 18 (section 6.1) showed that a reaction occurred over the duration of one hour minutes that caused the plasmon resonance to vanish in the UV-Vis spectra of sample EX13-High_Ag-0.2\%_H\(_2\)O. In contrast figure 21 shows the UV-Vis evolution of sample EX10-High_Ag-10\%_H\(_2\)O.
Figure 21: UV-Vis evolution of sample EX10-High_Ag-10\%_H\_2O. In comparison to sample EX13-High_Ag-0.2\%_H\_2O, whereby the plasmon resonance disappeared after 1 hour, the plasmon resonance in sample EX10- High_Ag-10\%_H\_2O was present for up to 96 hours and possibly longer, providing strong evidence that water stabilises the nanoparticles to some degree.

In comparison to sample EX13-High_Ag-0.2\%_H\_2O, the initial UV-Vis spectrum of sample EX10- High_Ag-10\%_H\_2O at $t = 0$ minutes showed a plasmon resonance with a peak absorbance intensity of 0.32 at a wavelength of 484 nm. Sample EX13-High_Ag-0.2\%_H\_2O had a peak plasmon resonance intensity of 0.32 at a wavelength of 494 nm at $t = 0$ minutes (see figure 19). Remarkably, whereas the plasmon resonance of sample EX13-High_Ag-0.2\%_H\_2O disappeared after 1 hour, that of sample EX10- High_Ag-10\%_H\_2O remained for the entirety of the investigation of 96 hours (4 days). As their plasmon resonances are of comparable intensity, and (with the exception of the addition of water to EX10) they were made following the same method to give high silver content, one can conclude that their silver content was approximately equal. It therefore appears the addition of 10\% water extended the lifetime of the plasmon resonance by an exceptional factor of approximately 100 times.
As seen from figure 21, over time, the plasmon resonance of sample EX10-High_Ag-10%_H₂O varied in intensity, whilst it also gradually shifted to longer wavelength, and broadened. Further analysis, using the graphical interpolation method (described in section 5) revealed an interesting trend in the peak plasmon resonance absorption evolution, as shown in figure 22 below.

**Figure 22:** The peak intensity of the plasmon resonance of sample EX10-High_Ag-10%_H₂O decayed exponentially within an initial period of 60 minutes but then grew exponentially over a period of days. The time constant for the initial decay was 27 minutes, and for the subsequent growth was 1995 minutes, approximately 1.4 days. Clearly two reactions occurred as the nanoparticles sample evolved.

Figure 22 shows how the peak plasmon resonance absorbance varied over a four day period. The inset shows the evolution over the first 60 minutes. Whilst not apparent from the figure 21, graphical interpolation analysis appeared to reveal two reactions. Firstly, the peak plasmon resonance absorbance decayed exponentially with a time constant of 27 minutes. Secondly, over the subsequent days, the absorption intensity recovered to almost that of its initial state, with a time constant of 1995 minutes. Such timing could imply fast dissolution of nanoparticles and then slower aggregation. It is possible that water etched the metallic nanoparticles, causing their quantity, and hence
absorbance to decrease. These etched particulates could then recombine causing the absorbance to grow again. Regardless of the reactions responsible for the change in intensity, water considerably changed the reactions that occurred. As opposed to an avalanche-type decay of the plasmon resonance, the graphical interpolation analysis shows that the plasmon resonance decayed gradually and then subsequently grew. Subsequent to the two reactions, the absorbance intensity stabilised lending strong evidence that due to the additional water content, the samples became colloidally stable. One can conclude with great confidence that water prolongs the plasmon resonance of the nanoparticles.

Figure 23 shows how the peak wavelength of the plasmon resonance shifted over time for sample EX10-High_Ag-10%_H₂O. Again, another exponential trend is observed. This shift in wavelength suggests a change is occurring in the sample. Possibilities of which include a change in nanoparticle size, a change of environment or a change in intrinsic properties. Additionally, the time constant for this reaction, 56 minutes is comparable in magnitude to the time constant of the initial decay in absorption intensity, which was 27 minutes. Hence, it is possible the cause of the plasmon resonance is related to the cause in its redshift.
6.4.2 Comparing Sample EX16 (Low Silver, 10% Water) to Sample EX10 (High Silver, 10% Water)

Sample EX16-Low_Ag-10%_H2O was produced under the same conditions as sample EX10-High_Ag-10%_H2O, with silver atoms sputtered onto a mixture of 10% water and 90% ethanol. As previously shown however, sample EX16 had a lower concentration of silver due to intermittent production (see figure 15), and therefore the initial plasmon resonance intensity was weaker, with an intensity of 0.12 at a wavelength of 458 nm. Nevertheless, the same results were observed: water prolongs the lifetime of the plasmon resonance, up to 18 hours, and for the duration of the investigation (figure 24). The spectrum also broadened over time, and shifted to the longer wavelengths. Again, the intensity decreased slightly before subsequently increasing and plateauing (figure 25), lending further evidence to suggest water improves the colloidal stability of the nanoparticle samples. Figure 26 shows how the peak wavelength of sample
EX16-Low_Ag-10\%_H_2O shifted to longer wavelengths exponentially, with a time constant very similar to sample EX10-High_Ag-10\%_H_2O.

![UV-Vis Evolution of Ex16 Ag-Ethanol (10\% H_2O, Low Silver Concentration)](image)

**Figure 24:** UV-Vis evolution of sample EX16; a second sample of silver nanoparticles suspended in ethanol with 10\% water. Sample EX16 had a comparatively low concentration of silver with respect to sample EX10-High_Ag-10\%_H_2O, hence the weaker plasmon resonance intensity (0.12 at 458 nm). Nevertheless, the same results were observed: water prolongs the lifetime of the plasmon resonance for the duration of the investigation; the spectrum broadened over time, and shifted to the right.
Figure 25: The peak intensity of the plasmon resonance of the low silver sample, sample EX16-Low_Ag-10%_H₂O behaved in a similar fashion to sample EX10-High_Ag-10%_H₂O. The absorption intensity of sample EX16 first decayed exponentially with a time constant of 26 minutes, and then grows with a time constant of 362 minutes.
Figure 26: The peak wavelength of the plasmon resonance of sample EX16-Low_Ag-10%_H2O shifted exponentially to longer wavelengths over time according to $531 - 59e^{-x/59}$. The time constant of the wavelength shift, 59 minutes, is comparable to the wavelength shift of sample EX10-High_Ag-10%_H2O, which was 56 minutes.

Comparing the time constants for the evolution of the plasmon resonances of samples EX10-High_Ag-10%_H2O and EX16-Low_Ag-10%_H2O several interesting observations can be made. Firstly, the time constants for the initial decay in absorption intensity are comparable; 27 minutes for sample EX10-High_Ag, as shown in figure 22, and 26 minutes for sample EX16-Low_Ag, as shown in figure 25. Secondly, the time constants for the redshift in wavelength are comparable; 56 minutes for sample EX10-High_Ag, shown in figure 23, and 59 minutes for sample EX16-Low_Ag, shown in figure 26. Consequently, this suggests that the reactions which occurred were independent of silver content. The time constants for the subsequent growth in absorbance intensity however, differed; 1995 minutes for sample EX10-High_Ag-10%_H2O as shown in figure 22, compared to 362 minutes for sample EX16-Low_Ag-10%_H2O as seen in figure 25. This slower evolution suggests an increased quantity of silver results in
slower evolution, which agrees with the result from our 0.2% water samples, EX9-High_Ag-0.2%_H2O and EX13-High_Ag-0.2%_H2O, shown in section 7.1.

6.4.3 Comparing Sample EX14 (1% Water, Low Silver Concentration) to Samples EX10 and EX16 (10% Water)

Figure 27 shows the UV-Vis Spectra over time of sample EX14-Low_Ag-1%_H2O, silver nanoparticles formed in a solution of 99% ethanol and 1% water. With just 1% water added, again, the same result occurred: the water prolonged the lifetime of the plasmon resonance. In this instance, with the presence of just 1% water, the lifetime of the plasmon resonance is extended for a remarkable 14 days. The spectrum also broadened over time, and shifted to the right. This could be explained if the formation of the silver hexahydrate cation is the reaction, possibly stabilising single silver ions in solution for long periods and dramatically decreasing the rate of aggregation (or stabilising the rate, and size, of the aggregate at any given time from t = 0).

**Figure 27:** Evolution of UV-Vis Spectra of sample EX14-Low_Ag-1%_H2O. In comparison to sample EX9-High_Ag-0.2%_H2O, the inclusion of just 1% water during production has a dramatic effect on the lifetime of the plasmon resonance; it is still present after 14 days.
Using the graphical interpolation method to measure the intensity of the plasmon resonance of sample EX14-Low_Ag-1\%_H\textsubscript{2}O, yet another interesting result is produced. Within the first 24 hours, the peak intensity of the plasmon resonance absorbance decayed in much the same way as the previous water samples (samples EX10-High_Ag-10\%_H\textsubscript{2}O and EX16-Low_Ag-10\%_H\textsubscript{2}O) albeit with a longer time constant (180 minutes, compared to 27 minutes and 26 minutes respectively). In the proceeding days, however, the plasmon resonance continues to decay exponentially with a time constant of 5810 minutes, as opposed to increase in intensity.

**Figure 28:** The peak intensity of the plasmon resonance of sample EX14-Low_Ag-1\%_H\textsubscript{2}O, silver atoms sputtered onto a solution of 99\% ethanol, 1\% water, decayed at first in a similar way to the 10\% water samples. The time constant of which is 180 minutes. In the following days however the plasmon resonance intensity continued to decrease in intensity, according to the equation $y = 0.025e^{-x/180} + 0.018$. This is in contrast to the 10\% water samples (samples EX10-High_Ag-10\%_H\textsubscript{2}O and EX16-Low_Ag-10\%_H\textsubscript{2}O) which subsequently grow in absorbance intensity.

As can be seen from figure 28, the plasmon resonance absorption for sample EX14-Low_Ag-1\%_H\textsubscript{2}O continued to decrease in intensity with a time constant of 5810 minutes, following the initial decay. In contrast, for the 10\% water samples (samples
EX10-High_Ag-10\%_H_2O and EX16-Low_Ag-10\%_H_2O) the plasmon resonance absorbance actually grew in intensity. Consequently, it appears the evolution of the plasmon resonance is correlated to the water content of the sample. With 0.2\% water, the plasmon resonance disappeared. With 1\% the plasmon resonance decayed in intensity, and the decay persisted. With 10\% water the plasmon resonance initially decayed in intensity, but then subsequently grew. It appears with increasing water content, we actually change the reactions that occur, hence change the formation of nanoparticles.

Figure 29 presents the results for how peak wavelength of the plasmon resonance of sample EX14-Low_Ag-1\%_H_2O evolved over time. The time constant of the wavelength shift for sample EX14, was 2073 minutes. This was significantly longer than the 10\% water samples, 59 minutes for EX16-Low_Ag-10\%_H_2O and 56 minutes for EX10-High_Ag-10\%_H_2O respectively. Unfortunately at this stage of the investigation, there is not a feasible hypothesis to explain this result. The trend would have suggested that the time constant for the wavelength shift would be of the same order of magnitude or less than the 10\% water samples. Further investigations into 1\% water samples would be required to explain why the redshift of the peak wavelength is so comparatively lengthy.

![Redshift of Peak Plasmon Resonance in EX14 Ag-Ethanol (1\% H_2O)](image_url)

**Figure 29:** The peak wavelength of the plasmon resonance of sample EX14-Low_Ag-1\%_H_2O shifts exponentially to longer wavelengths over time according to 561 – 79e^{x/2073}.
6.4.4 Summary of water dependency results

With the absence of water, the plasmon resonance rapidly disappeared. Therefore, one can conclude in the absence of water, the nanoparticles are not colloidally stable. Figure 30 presents a summary of the samples discussed so far. Note, since the plasmon resonance of the nanoparticles disappeared so readily in the pure HPLC ethanol samples a time constant for the decay is not calculated. In the presence of 1% water, the nanoparticles’ plasmon resonance persisted for up to 14 days, albeit it decays exponentially. However, the time constant for this decay is 5810 minutes, or approximately 4 days, and are therefore in comparison, more colloidally stable. For 10% water samples, the plasmon resonance absorption intensity decayed rapidly at first, but then grew steadily back to its initial intensity. This suggests two reactions occurs, and after a period of time, since the plasmon resonance intensity stabilises, the nanoparticles become colloidally stable after the second reaction.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Silver concentration (no. of molecules)</th>
<th>Water Concentration (no. of molecules)</th>
<th>Initial Plasmon Resonance Decay Time Constant</th>
<th>Subsequent Plasmon Resonance Decay/Growth Time Constant</th>
<th>Plasmon Resonance Wavelength Time Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>EX9</td>
<td>$1.39 \times 10^{19} \pm 0.35 \times 10^{19}$</td>
<td>$6.68 \times 10^{19}$ (0.2% H$_2$O)</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>EX13</td>
<td>$1.39 \times 10^{19} \pm 0.35 \times 10^{19}$</td>
<td>$6.68 \times 10^{19}$ (0.2% H$_2$O)</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>EX10</td>
<td>$1.39 \times 10^{19} \pm 0.35 \times 10^{19}$</td>
<td>$3.34 \times 10^{21}$ (10% H$_2$O)</td>
<td>27 minutes</td>
<td>1995 minutes *Growth</td>
<td>56 minutes</td>
</tr>
<tr>
<td>EX16</td>
<td>$6.9 \times 10^{18} \pm 1.73 \times 10^{18}$</td>
<td>$3.34 \times 10^{21}$ (10% H$_2$O)</td>
<td>26 minutes</td>
<td>362 minutes *Growth</td>
<td>59 minutes</td>
</tr>
<tr>
<td>EX14</td>
<td>$6.9 \times 10^{18} \pm 1.73 \times 10^{18}$</td>
<td>$3.34 \times 10^{20}$ (1% H$_2$O)</td>
<td>180 minutes</td>
<td>5810 minutes *Decay</td>
<td>2073 minutes</td>
</tr>
</tbody>
</table>

**Figure 30:** Summary of results showing how the nanoparticles’ colloidal stability is dependent on water
The time constants for sample EX14, which contains 1% water, do not fit in with the main results. For low silver concentration, one might expect faster evolution, but as can be seen from figure 27, this is not the case for the initial plasmon resonance absorption decay, the subsequent plasmon resonance absorption decay or the redshift in wavelength. Thus, whilst it is shown that the addition of water appears to improve colloidal stability, evidently there is a complicated relationship between silver concentration and water concentration, and in this experiment it is difficult to disentangle the two variables; this is a matter that would merit future investigations using techniques that is beyond the scope of our current work.

6.4.5 Sample EX13 (High Silver, 0.2% Water): Adding Water Post Production

As previously discussed, sample EX13-High_Ag-0.2%_H2O was produced by sputtering silver atoms onto pure HPLC-grade ethanol which contains 0.2% water. As an additional experiment, once manufactured, the sample was also serially diluted with water. Diluting the sample four-fold with water yielded a sample that was 75% water; diluting this solution four-fold further yielded a sample with 94% water. The purpose of this experiment was to investigate whether adding water post production would affect the stability of the plasmon resonance. Figure 31 shows the results.
Figure 31: UV-Vis Spectra of sample EX13-High_Ag-0.2%_H₂O (uppermost graph) and subsequent dilutions with water (centre and lowermost) over time. Adding ultrapure water to sample EX13 post production stabilised the plasmon resonance. It was still present after 96 hours when diluted four times with water, and after 140 minutes when diluted 16 times with water. Compared to the original sample, the plasmon resonance completely disappeared after only 120 minutes.

In the uppermost section of figure 31, is the evolution of sample EX13-High_Ag-0.2%_H₂O. As shown previously (figure 18) the plasmon resonance, which was of an initial intensity of 0.32, disappeared within 2 hours. In comparison, the plasmon resonance in the sample which was diluted four-fold with water, 75% water (centre section) was still obvious after 2 hours, and was, in fact, perceptible after as long as 96 hours. This result provides clear evidence that water has a stabilising effect on the nanoparticles. Adding water post production to a sample that was produced in pure HPLC grade ethanol prolonged the plasmon resonance by approximately 50 times. Diluting the sample a further four-fold, still yielded a plasmon resonance. After two hours, the plasmon resonance was evident, and much more pronounced than the undiluted sample. After 96 hours a plasmon resonance could not be detected, however, the signal was weak due to the extent of the dilution. Note that the scale in each section of figure 31 differs due to the difference in signal intensity. From this result, together with the results
summarised in figure 30, we can confidently conclude that adding water increases the colloidal stability of the nanoparticles.

### 6.5 Absorbance Intensity and Evolution of 277 nm Peak Depends Upon Silver Concentration and Water Concentration

In each of the nanoparticle samples produced via the liquid jet technique, a second interesting feature, which is referred to as the ‘shoulder’ was observed. It peaked in intensity at 277 nm and at first, decreased in intensity over time. It then however, grew considerably in intensity, and looked similar to a shoulder, hence its nomenclature. Although a supporting theory to explain the feature does not necessarily exist, its evolution was monitored regardless as an indicator of sample evolution. To analyse the magnitude of this ‘shoulder’ feature, the peak absorption intensity was taken to be the peak absorbance as measured from zero. This was done because there is not a clear ‘obvious’ component that can be subtracted to leave an ‘absolute’ absorption intensity for the shoulder. Of course, it is recognised this could introduce some ambiguity when comparing time constants for the shoulder feature to the plasmon resonance; however, this method is accepted for the time being and its limitations considered later.

Sample EX7-High_Ag-1%_H2O contained a large concentration of silver, because the sample was manufactured prior to the development of the umbrella shield (see section 5.2.2). Figure 32 shows the sample’s UV-Vis spectra as it evolves over time.
Figure 32: UV-Vis spectra of sample EX7-High_Ag-1%_H₂O, centred on the feature at 277 nm. The inset shows how the intensity of the feature at 277 nm changed over time. There was an initial exponential decay consistent with the equation $y = 0.72 + 0.3e^{-x/19}$ within the first 60 minutes, and then a subsequent exponential growth over a period of 24 hours consistent with $y = 1.39 - 0.69e^{-x/668}$.

In figure 32, at $t = 0$ minutes, a maximum in the sample EX7’s spectroscopy spectrum is observed at 277 nm, with an absorbance intensity of 0.99. Over a period of 60 minutes, this maximum decreases exponentially to an intensity of 0.74. The time constant of this exponential decay is 19 minutes. Over the subsequent 24 hours, the maximum grows exponentially, with a time constant of 668 minutes. From the results, it is hypothesised that two reactions are occurring. An initial exponential decay, that possibly occurs for longer than the observed duration (and one which is possibly consistent with the decrease in intensity of the overall spectrum) and a second reaction that is responsible for the exponential growth which occurs simultaneously, but is only evident at $t = 2$ hours. Regardless, the result from this phenomenological study was that a peak/shoulder emerged at 277 nm within a period of 24 hours, peaking at an absorbance of 1.37. One can be confident that for such an observation, a reaction involving the nanoparticles must be occurring.
Sample EX14-Low_Ag-1%_H2O, whilst produced under the same conditions as sample EX7-High_Ag-1%_H2O contained a much lower quantity of silver, because, as previously explained, atomic silver production in this case was intermittent. Nevertheless, the evolution of the 277 nm was similar for the two samples. Figure 33 shows the UV-Vis spectrum of sample EX14. In comparison to the previous ‘high silver’ EX7 spectra, the initial absorbance intensity at 277 nm is 0.50. This absorbance intensity then decays exponentially, with a time constant of $\tau = 271$ minutes before subsequently growing to 0.47 with a time constant of 6506 minutes. To compare, the same feature in sample EX7-High_Ag-1%_H2O decayed with a time constant of $\tau = 19$ minutes before growing to an absorbance of 1.37, with a time constant of 668 minutes. Sample EX14 has a low concentration of silver, hence a correlation can be identified; a decreased silver concentration results in a lower absorbance at 277 nm, and a slower evolution. The inset illustrates how sample EX14 appears to follow the same evolution as sample EX7 just at a slower rate.
Figure 33: UV-Vis spectra of sample EX14-Low_Ag-1%_H₂O, showing the characteristic ‘shoulder’ feature at 277 nm. In the first 20 hours, the same exponential decay at 277 nm as seen in sample EX7-High_Ag-1%_H₂O was observed but with a much larger time constant, \( \tau = 271 \) minutes compared to \( \tau = 19 \) minutes for sample EX7. The absorbance intensity then grew, to an intensity of 0.47, with a time constant of 6506 minutes.

Samples EX10-High_Ag-10%_H₂O and EX17-Low_Ag-10%_H₂O were silver nanoparticle samples produced in 10% water, 90% ethanol. Sample EX10 contained a large quantity of silver and sample EX17 contained a low quantity of silver. Figures 34 and 35, respectively, show the UV-Vis spectra for sample EX10 and sample EX17. Sample EX10-High_Ag-10%_H₂O has an absorbance = 1.70 at 277 nm, and a time constant of growth, \( \tau = 332 \) minute and sample EX17-Low_Ag-10%_H₂O has an absorbance = 0.59 at 277 nm, and a time constant of growth, \( \tau = 1633 \) minutes. Interestingly there does not appear to be an initial decrease in absorption intensity at 277 nm for either sample. This could be due to insufficient measurements; however, it could also be due to a large excess of water, forming silver hexahydrate cations. Nevertheless, this reaffirms the results from the plasmon resonance investigation; water increases the colloidal stability.
Figure 34: UV-Vis spectra of EX10-High_Ag-10%_H2O, 10%. Sample EX10 contains a comparatively high concentration of silver, and consequently the ‘shoulder’ observed at 277 nm evolves more rapidly; exponential growth within 24 hours was observed, with a time constant of 332 minutes. The absorbance intensity increases from 1.16 to 1.70. The initial exponential decay in absorbance intensity at 277 nm as seen in the 1% water samples is not observed. It is possible this is due to a large excess of water.
Growth of peak at 277 nm: EX17 Ag-Ethanol (10% H₂O) - Low Silver Concentration

**Figure 35**: UV-Vis spectra of sample EX17-Low_Ag-10%_H₂O. In comparison to sample EX10-High_Ag-10%_H₂O, sample EX17 contained a nominal amount of silver. Consequently, the peak at 277 nm, evolves at a much slower exponential rate, τ = 1663 minutes. The absorbance at 277 nm increases from 0.28 to 0.59. Similar to sample EX10, we do not see an initial exponential decrease in intensity, possibly due to an increase of water.

Comparing the four samples discussed, several trends can be identified. Firstly, it appears a higher silver concentration results in higher absorbance intensity at 277 nm, initially, and once the sample has matured. Consequently, a higher silver concentration must promote the growth of the particles responsible for this peak. Figure 36 shows how the absorbance at 277 nm correlates with silver concentration. Secondly, a higher silver concentration increases the rate at which the absorbance intensity at 277 nm initially decreases and then subsequently grows, see figure 37. Hence, one can conclude that silver promotes both processes. This subsequent growth in absorbance at 277 nm, however, is the inverse of how the plasmon resonance evolved. For the plasmon resonance results, it was suggested an increased silver concentration resulted in slower evolution. Here it seems the opposite is true in terms of the evolution of the 277nm peak, with an increased silver concentration resulting in quicker evolution of this feature. Thus, it is possible increased silver content promotes the evolution of the 277 nm peak, whilst it impedes the
evolution of the plasmon resonance. This conclusion would be consistent with these features originating from different processes within the samples, both of which are affected by silver concentration but in differing ways.

Figure 36: The absorbance intensity of the 277 nm feature increases with increasing silver concentration. Although it is not possible to quantitatively state the concentration of silver in each sample, although estimates are provided in figure 15, it was possible to distinguish with confidence, which samples have a high silver concentration, and which do not. For all samples, however, it can be stated that the water concentration was in excess of the silver concentration.
Figure 37: The rate at which the absorbance of the ‘shoulder’ feature at 277 nm changes correlates with silver concentration. With increasing silver concentration there results a faster change, and hence shorter time constant. As can be seen, the initial decay in absorbance intensity for the 1% water samples is quicker for high silver concentration sample; sample EX7-High_Ag-1%_H2O compared to EX14-Low_Ag-1%_H2O. Similarly, the subsequent growth in intensity is quicker for sample EX7 compared to EX14. For the 10% water samples there is no initial decay in absorbance, however, similar to the 1% water samples, the absorbance increases quicker for the high silver sample; EX10-High_Ag-10%_H2O compared to EX17-Low_Ag-10%_H2O.

Figure 37 also reveals that the time constants for the evolution in absorbance, are larger for the 1% samples than the 10% water samples ($\tau_{\text{EX14-Low_Ag-1%_H2O}} > \tau_{\text{EX17-Low_Ag-10%H2O}}$ and $\tau_{\text{EX7-High_Ag-1%_H2O}} > \tau_{\text{EX10-High_Ag-10%H2O}}$). In other words, the evolution is slower when there is less water. This suggests that water content is relevant to the absorbance at 277 nm.
Figure 38 shows the UV-Vis spectra of sample EX13-High_Ag-0.2%_H2O shown also in figure 18 and figure 31. We observe a plasmon resonance at $t = 0$ minutes. This quickly disappears due to the absence of water. From before, it was concluded that water increases the colloidal stability of the nanoparticles. For the 0.2% water sample, an obvious exponential decay in the absorbance at 277 nm is observed, with a time constant of 17 minutes (see inset, figure 38). The time constant for the subsequent growth is 3973 minutes. This is substantially longer than both the 1% and 10% water, high silver concentration samples. Note the absorbance intensity does not increase to greater than its original value, unlike the 1% and 10% water samples. Figure 39 shows how the rate of the subsequent growth of absorbance intensity at 277 nm changes with water concentration.
Figure 39: The rate at which the absorbance intensity grows at 277 nm, increases with increasing water content. For 0.2% water (high silver concentration), the absorbance changes slowly, with a time constant of 3973 minutes. Whereas for 10% water (high silver) the absorbance changes much faster, $\tau = 332$ minutes. Therefore, we can conclude that water also promotes the production of the particles responsible for absorbance at this 277 nm.

From Figure 39, it is evident that the source of the absorbance at 277 nm is also dependent on water. With increasing water concentration, the time constant of the growth in absorbance intensity shortens. Because the absorbance at 277 nm increases, it suggests the concentration of nanoparticles causing it increases. Hence, water must in some way be related to the responsible particles if increasing water content promotes a faster increase in absorbance intensity.

From the results presented in this section, two things can be concluded. Firstly, with an increased concentration of silver, the absorbance of the 277 nm peak increases, along with the reaction rate of the exponential decay and growth of absorbance intensity. Secondly, with increasing water content, the time constant for the growth in absorbance shortens. Unfortunately, the two variables are difficult to separate, and hence a quantitative result to accompany this conclusion cannot be provided. Nevertheless, such a result supports the hypothesis that silver hydroxide compounds, for example AgOH, could be responsible for this peak.
7 CONCLUSION

In this thesis, I investigated how interactions between metal and solvent molecules affected the formation of nanoparticles produced using the liquid jet technique. Specifically, I assessed how the water concentration affects the colloidal stability of the nanoparticles. In all previous investigations employing this method of production, the samples produced have been subject to contamination from water vapour. If we are to gain the level of understanding necessary to fully exploit the potential offered by liquid synthesis methods of producing nanoparticles, then it is essential that one investigates what role, if any, that water may have played in the formation of the nanoparticles. By modifying the experimental set-up, I was able to improve the purity of our samples by an order of magnitude, allowing water to be reintroduced in a controlled manner. The results show that water fundamentally changes the interactions between metal and solvent.

Using primarily UV-Vis spectroscopy, the stability and evolution of nanoparticles produced in the liquid jet with varying concentrations of silver and water was probed. The results show that in the absence of water, silver nanoparticles, produced by sputtering silver onto a liquid ethanol jet, undergo an avalanche-type reaction, which causes the clusters to lose their stability in solution, exhibited by the disappearance of the surface plasmon feature from their UV-vis spectra over time. In contrast, in the presence of water however, the results show that the nanoparticles are apparently more stable, and in particular retaining the observed plasmon resonance for prolonged periods. This is a result that may be of great interest for the practical use of metal nanoparticles produced in solution, particularly for plasmonic applications.

The challenges posed in investigating even this apparently simple nanoparticle system within the existing experimental setup prevented exact determination of the apparently complex reactions that occurred during the evolution of our samples in solution; however, the results suggest a number of interesting possibilities. It is possible the water causes fast dissolution of nanoparticles, and then slower aggregation, and thereby increases the colloidal stability of the nanoparticles. In all cases where water was
present, it was shown that the nanoparticles retained their plasmon resonance in the UV-spectrum for the duration of investigation.

In addition to the silver plasmon resonance, our UV-vis results revealed a further interesting spectral feature of the samples at 277 nm, which exhibited a differing evolutionary profile to that of the silver plasmon resonance. Higher concentration of silver resulted in both a stronger plasmon resonance and a stronger absorption at 277 nm, however, in contrast to the plasmon resonance, the time constant associated with the growth in absorbance intensity at 277 nm also correlated to the water content of the samples, with decreasing time constant with increasing water content. Consequently, because it can be concluded absorption at 277 nm correlates with both water concentration and silver concentration, we hypothesise AgOH may be responsible for the peak. This is an interesting result that merits further investigation, for example through using drying agents to eliminate the presence of water from our technique completely.

In addition to the above observations, in this investigation it was also shown by pipetting different layers of the sample into the UV-Vis spectrometer (section 7.3) that an absorbance appearing at 240 nm in our UV-Vis measurements may possibly be attributed to OH ions present in the samples. Unfortunately, in all of the UV-Vis measurements in this investigation, the absorbance of the 240 nm was too high to allow reliable comparisons. It would therefore be useful in future investigations to perform dilution experiments. This would allow one to establish if the peak at 240 nm varied in intensity with water content, providing further evidence that OH ions are the responsible source. Energy dispersive x-ray spectroscopy and x-ray photo electron spectroscopy would also be useful tools that would merit future use for confirming the identity of the particles responsible for the peaks identified in the UV-Vis spectrums.

In summary, by developing certain simple modifications to the liquid jet set up, and employing UV-vis spectroscopy, it was demonstrated water plays a key role in the formation and evolution of silver nanoparticles in ethanol. Whilst the limitations of the experimental set-up prevented exact determination of the complex series of reactions taking place within this system that were revealed by this investigation, a number of interesting results were identified that may be key to the future use of this system in practical applications.
8 Appendices

Appendix 1: Size Distribution of Silver Nanoparticles Recorded from TEM Survey Images........................................................................................................73

Appendix 2: Size Distribution of Silver Nanoparticles Sputtered onto Silica Nanospheres........................................................................................................74

Appendix 3: Calculating the Area of the Liquid Jet and the Surface of the Steel Cold Trap...........................................................................................................75
APPENDIX 1: SIZE DISTRIBUTION OF SILVER NANOPARTICLES Recorder FROM TEM SURVEY IMAGES.

Figure 40: Size distribution of silver nanoparticles recorded from TEM survey images. The solid lines are log-normal fits. For low silver loading, i.e. deposition onto only the liquid jet (JOD) the nanoparticles had a median diameter of 2.0 ± 0.7 nm. For high loading, i.e. jet co-deposition the nanoparticles had a median diameter of 3.8 ± 3.0 nm.
APPENDIX 2: SIZE DISTRIBUTION OF SILVER NANOPARTICLES SPATTERED ONTO SILICA NANOSPHERES

Figure 41: (Mcnally, Galinis, Youle, Chantry and von Haeften. 2016). (a) (b) and (c) show example Transmission Electron Microscopy survey images, as imaged by myself, used to form size distributions (d). (a) shows nanoparticles produced by jet-co-deposition (JCD); (b) shows nanoparticles produced by jet-only-deposition (JOD); (c) shows nanoparticles produced by jet-co-deposition onto silica nanospheres. The larger, lighter circles are silica particles, the smaller black particles are silver nanoparticles. The same data shown in (d) is plotted in (e) to show the median (horizontal centre line), 25/75 percent limits (box), 99th percentile (circle) and minimum/maximum limits (vertical line ends). As can be seen from (e) there are no silver nanoparticles greater than 20 nm, hence we conclude the silica nanospheres limit the growth of the silver nanoparticles.
APPENDIX 3: CALCULATING THE AREA OF THE LIQUID JET AND THE SURFACE OF THE STEEL COLD TRAP

We approximate the jet to be a divergent beam of micro-droplets from the point at which it leaves the capillary. We also approximate this divergent of micro-droplets as an opaque surface, i.e. the liquid jet traps one hundred percent of the metal atoms that interact with. Consequently the ‘visible area’ of the liquid jet that the silver atoms interact with is represented as two-dimensional divergent surface, figure 42.

![Figure 42](image)

**Figure 42:** The liquid jet is approximated as a divergent cone as it exits from the capillary. Consequently the projected ‘visible’ area of the liquid jet the metal atoms can then interact with takes the form of a trapezium, the dimensions of which are shown above (diagram not to scale).

Depending on the expansion conditions, the solvent jet diverges as the solvent sprays from the 50 μm capillary. This is because in the vacuum, which is of the order $10^{-2}$ mbar, there are minimal opposing forces keeping the jet aligned. Frozen solvent spray on the cold-trap suggests it diverges to a width of approximately 3 mm. Therefore, the width of the jet is given as $a = 50 \mu m$, expanding to $b = 3$ mm. The length of the jet, which is exposed to the metal atoms as it travels through the vacuum chamber is approximately 10 cm. Consequently, the area of the liquid jet, exposed to the vapour of atoms is approximately:

$$\text{Area of Jet} = \frac{a+b}{2} \times l = 1.53 \times 10^{-4} \text{ m}^2$$

If sputtered material also deposits directly onto the frozen solvent surface on the cold trap, then there exists a larger surface area that is coated with vaporised atoms. The dimensions of the window of the cold trap are 1 cm by 4 cm, and hence the additional area to which atoms can deposit is 0.0004 m².
9 Bibliography


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Chapter 0: