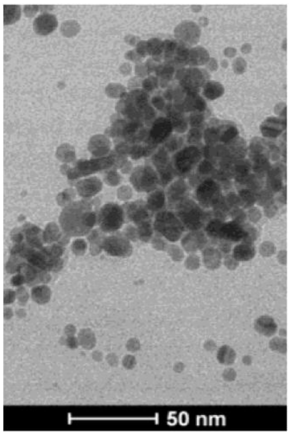
Application Note 40:

Preparation of Silver Nanoparticles under Continuous Flow Conditions

Produced by Vapourtec

Abstract

This application note illustrates the use of the Vapourtec E-Series system to nanoparticles under continuous flow conditions. Two classes of silver nanoparticles are reported.



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Background

Continuous flow is finding applications not only in organic synthesis but also for inorganic chemistry. One example is the preparation of metal nanoparticles. Metal nanoparticles are used in a wide range of applications.[1] In medicine, they can be used as antioxidants to remove oxygen free radicals that are present following a traumatic injury or can assist in bone growth around dental or joint implants. In the materials industry they can be used to provide a barrier to gasses or moisture in plastic films used for packaging or can be dispersed in industrial coatings to protect wood, plastic, and textiles from exposure to UV radiation. Silver nanoparticles have been impregnated in fabric to kill bacteria, making clothing odor-resistant. From an environmental perspective, metal nanoparticles can be used as catalysts to break down oil in the ground or volatile organic pollutants in the air.

The properties of metal nanoparticles are highly dependent on size and morphology, so ensuring consistency from batch to batch is paramount. Flow chemistry brings the advantages of precise control over experimental conditions (temperature, pressure, and residence time) and essentially limitless scale. As such, it is often the method of choice for production of nanoparticles. There are literature examples of silver, gold, palladium, platinum, iron, and cobalt nanoparticles being prepared this way.

The Vapourtec E-Series system is a simple and robust flow chemistry unit. The unique pumping system allows reliable and smooth pumping across a wide range of flow rates. The self-priming mechanism allows this system to be up and running in a matter of minutes. This application note demonstrates the capability of the E-Series for the production of two classes of silver nanoparticles.

The first approach, based on a batch method developed by Mirkin[2] and later modified by Kitaev,[3] involves the use of sodium borohydride to reduce silver nitrate. As the silver ions are reduced, silver atoms begin to aggregate, forming nanoparticles in the presence of surface stabilizing and shape- and size-modifying agents. Sodium citrate is used both as a buffer to maintain a neutral or weakly basic pH of the solution and to charge stabilize the silver nanoparticles. Hydrogen peroxide is used to facilitate the formation of shape-selected nanoparticles by serving as an etching agent. Finally, potassium bromide is added to the reaction to control particle size. Bromide ions bind strongly to the silver surface, forming silver bromide that arrests growth of the silver nanoparticle. By using different concentrations of bromide in the reaction, it is possible to vary the size of the final nanoparticles. The preparation of the nanoparticles is performed at room temperature.

The second approach, based on a batch method by Hasan,[4] uses polyethyleneglycol (PEG) to reduce silver nitrate to silver ions. Polyvinylpyrrolidone (PVP) is used as a capping agent to control nanoparticle size. Since the reaction of PEG with silver nitrate is relatively slow, when operating in batch the reaction mixture is heated to 90 °C in a water bath for up to 90 min. In flow, the reaction can be performed with a residence time of 5 min, operating at 120 °C.

Reactions were optimized and monitored using off-line UV-vis spectrophotometry. In the case of one of the samples, a transmission electron micrograph (TEM) was also obtained to confirm the formation of the nanoparticles.

Method

Preparation of silver nanoparticles using sodium borohydride as a reducing agent, hydrogen peroxide as an etching agent, and potassium bromide to control particle size.

Setup

The flow reactor was set up using the **E-Series** pump module as shown in Fig 1.

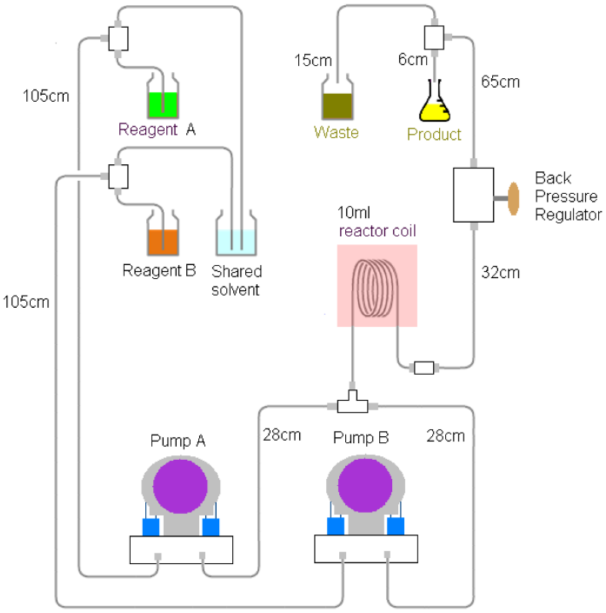


Fig 1: E-Series Setup.

A 10 mL PFA reactor was installed with a connecting tube in series with a manually adjustable back pressure regulator. The elution outflow was collected via the waste/collection switching valve.

Pump Tubing

It is to be noted that the V-3 pump used by the E-Series is based on the peristaltic principle, and so features a high performance fluoropolymer tube at its core. More than one pump tube type is available to ensure compatibility with the broadest possible range of solvents, so selection of the correct tube for a given application is critical.

A table showing recommended tube type compatibility with a wide selection of solvents, acids and bases is available both within the E-Series user manual and also built into the User Interface software. In this case blue tubing was used for both pumps.

Reagents

All reagents and solvents were used as purchased. The water used should ideally be Millipore grade (with >18.2 MΩ cm resistivity); however, acceptable results can be obtained using water purified by high-quality reverse osmosis. The solution of sodium borohydride must be prepared on the day of use. Decomposition occurs over time which negatively impacts the results.

Reagent A

Prepare the following solutions:

- 100 mL of a 3.75×10^{-4} M solution of sodium citrate [Place 0.011 g sodium citrate in a volumetric flask and dissolve in 100 mL water]
- 250 mL of a 3.75×10^{-4} M solution of silver nitrate [Place 0.016 g $AgNO_3$ in a volumetric flask and dissolve in 250 mL of water]
- 250 mL of a 5.0×10^{-2} M solution of hydrogen peroxide [Place 1.20 mL of 30% (10.4 M) H_2O_2 in a volumetric flask and add water to make up to 250 mL]
- 100 mL of a 1.0×10^{-3} M solution of potassium bromide [Place 0.012 g of KBr in a volumetric flask and add 100 mL water]

In a bottle labelled “Reagent A”, combine 50 mL of the sodium citrate solution, 125 mL of the silver nitrate solution, and 125 mL of the hydrogen peroxide solution. The quantity of potassium bromide solution can be varied, depending on the size of nanoparticles required: none (blue solution of nanoparticles, 64 nm average size), 20 μL (violet solution, 40 nm average size), 25 μL (orange solution, 35 nm average size), 40 μL (yellow solution, 10-30 nm average size).

Reagent B

250 mL of a 5.0 × 10-3 M sodium borohydride solution [Place 0.4729 g of $NaBH_4$ in a volumetric flask and dissolve in 250 mL of water]

System Parameters

System solvent:	Water
Reagent A:	Aqueous solution of sodium citrate, silver nitrate, hydrogen peroxide, and potassium bromide
Reagent B:	Aqueous solution of sodium borohydride
Flow rate A:	1.66 mL/min
Flow rate B:	0.34 mL/min
Reactor volume:	10 mL PFA reactor.
Reactor temperature:	Room temperature (25 °C)

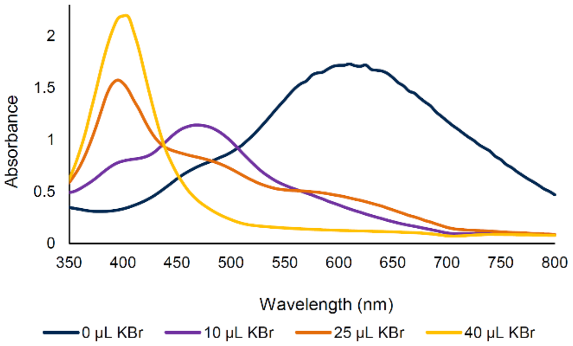
Back pressure regulator:	4 Bar set with the variable BPR

Reactions followed the sequence of events listed below:

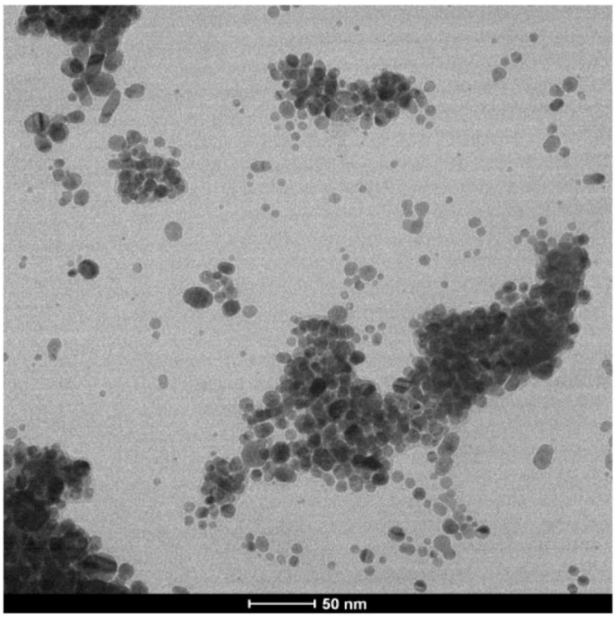
1. Priming the pumps with water: Both selection valves were set to ‘Solvent’ and the pumps were primed with water. This is done by selecting the “prime” function from the touchpad control.
2. Priming the pumps with reagents: The selection valve for line 1 was set to “Reagent”, the “prime” function selected, and the line connecting the valves to stock bottle 1 filled with **Reagent A.** The selection valve was set back to “Solvent” and water pumped through the lines using the “prime” function. The process was repeated with line 2, using **Reagent B** to fill the second reagent line.
3. Running the reaction: **Reagent A** was pumped at a flow rate of 1.66 mL/min and **Reagent B** was pumped at 0.34 mL/min. Only the steady state portion of the product mixture was collected so as to take into account the dispersion of the reaction segment.

Results

The distinctive colors of silver nanoparticles are due to the characteristic surface plasmon resonance peak between 400-450 nm. The wavelength of the plasmon absorption maximum in a given solvent can be used to indicate particle size. As the size decreases, so the wavelength of the plasmon absorption becomes more blue-shifted (decrease in wavelength). This is reflected in the UV-vis spectra of nanoparticles produced in continuous-flow.



A representative sample of nanoparticles was examined using transmission electron microscopy (TEM). A sample of silver nanoparticles from a freshly synthesized solution was prepared by drying a small drop on a carbon-coated 200-mesh copper grid. The TEM shows formation of nanoparticles. There is a degree of aggregation observed. This was due to the method of sample preparation used.



Scale-up

The reaction was performed as above, operating for 90 minutes continuously. Only the steady state portion of the product mixture was collected so as to take into account the dispersion of the reaction segment. Assay of the product showed that the reaction could be scaled without any issues.

The process followed the sequence of events listed below:

1) *Priming the pumps with water:* Both selection valves were set to 'Solvent' and the pumps were primed with water. This is done by selecting the prime function from the touchpad control and is fully automated.
2) *Priming the pumps with reagents:* The selection valve for line 1 was set to "Reagent", the "prime" function selected, and the line connecting the valves to stock bottle 1 filled with **Reagent A.** The selection valve was set back to "Solvent" and water pumped through the lines using the "prime" function. The process was repeated with line 2, using **Reagent B** to fill the second reagent line.
3) *Running the reaction:* **Reagent A** was pumped at a flow rate of 1.66 mL/min and Reagent B was pumped at 0.34 mL/min for a total time of 90 mins.

Method 2

Preparation of silver nanoparticles using polyethyleneglycol (PEG) as a reducing agent and polyvinylpyrrolidone (PVP) to control particle size.

Setup

The flow reactor was set up and equipped with tubing in the same way as in Method 1.

Reagents

All reagents and solvents were used as purchased. The water used should ideally be Millipore grade (with >18.2 MΩ cm resistivity); however, acceptable results can be obtained using water purified by high-quality reverse osmosis. Polyethyleneglycol with an average molecular weight of 6000 (PEG-6000) and polyvinylpyrrolidone K30 with an average molecular weight of 4000 were used.

Reagent A

Prepare the following solutions:

- A 20 % solution by weight of polyethyleneglycol [Dissolve 20 g of PEG-6000 in 80 mL water. To dissolve the PEG-6000 it is necessary to heat the solution to ~ 80 °C for a few minutes]
- A 20 % solution by weight of polyvinylpyrrolidone [Dissolve 20 g of PVP-K30 in 80 mL water. To dissolve the PVP-K30 it is necessary to heat the solution to ~ 80 °C for a few minutes]

In a bottle labelled "Reagent A", combine 50 mL of the PEG solution and 50 mL of the PVP solution.

Reagent B

100 mL of a 0.1 M solution of silver nitrate [Place 1.698 g $AgNO_3$ in a volumetric flask and dissolve in 100 mL of water]

System Parameters

System solvent:	Water
Reagent A:	Aqueous solution of PEG and PVP
Reagent B:	Aqueous solution of silver nitrate
Flow rate A:	0.75 mL/min
Flow rate B:	0.75 mL/min
Reactor volume:	10 mL PFA reactor.
Reactor temperature:	80-120 °C
Back pressure regulator:	6 Bar set with the variable BPR

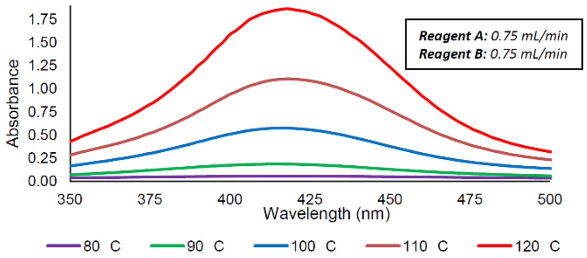
Optimization

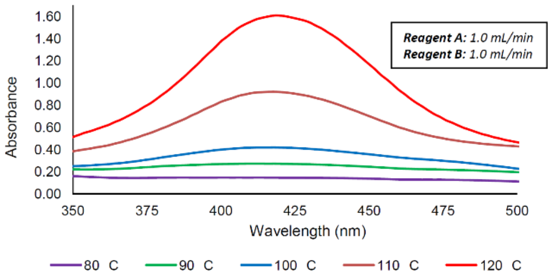
Reactions followed the sequence of events listed below;

1) *Priming the pumps with water:* Both selection valves were set to 'Solvent' and the pumps were primed with water. This is done by selecting the prime function from the touchpad control and is fully automated.
2) *Priming the pumps with reagents:* The selection valve for line 1 was set to "Reagent", the "prime" function selected, and the line connecting the valves to stock bottle 1 filled with **Reagent A**. The selection valve was set back to "Solvent" and water pumped through the lines using the "prime" function. The process was repeated with line 2, using **Reagent B** to fill the second reagent line.
3) *Running the reaction:* Reagent streams were flowed at rates varying from 0.75-1.0 mL/min and runs were performed at temperatures between 80-120 °C. Only the steady state portion of the product mixture was collected so as to take into account the dispersion of the reaction segment.

Results

Using UV-vis spectrophotometry as a tool, optimal reaction conditions were found to be when a flow rates of 0.75 mL/min for reagent A and reagent B was used and the mixture heated at a temperature of 120 °C.





Scale-up

The reaction was performed as above but at the optimal flow rate of 0.75 mL/min (Reagent A and Reagent B) and temperature of 120 °C, operating for a total of 90 minutes. Only the steady state portion of the product mixture was collected so as to take into account the dispersion of the reaction segment. Assay of the product showed that the reaction could be scaled without any issues.

Reactions followed the sequence of events listed below:

4) *Priming the pumps with water:* Both selection valves were set to 'Solvent' and the pumps were primed with water. This is done by selecting the prime function from the touchpad control and is fully automated.
5) *Priming the pumps with reagents:* The selection valve for line 1 was set to "Reagent", the "prime" function selected, and the line connecting the valves to stock bottle 1 filled with **Reagent A.** The selection valve was set back to "Solvent" and water pumped through the lines using the "prime" function. The process was repeated with line 2, using **Reagent B** to fill the second reagent line.
6) *Running the reaction:* Water was passed through the reactor coil at a flow rate of 1.5 mL/min (pump 1 = 0.75 mL/min, pump 2 = 0.75 mL/min). The flow reactor coil was heated to 120 °C. When at temperature,

Reagent A was pumped at a flow rate of 0.75 mL/min and **Reagent B** was pumped at 0.75 mL/min.

Conclusion

The work described here demonstrates the use of the Vapourtec E-Series for the preparation of metal nanoparticles in a safe, efficient and continuous manner.

Acknowledgements

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References

1. For background, see: (a) Vollath, D. *Nanoparticles - Nanocomposites Nanomaterials: An Introduction for Beginners,* Wiley-VCH, Weinheim, **2013.** (b) Schmidt, G. (Ed) *Nanoparticles: From Theory to Application,* Wiley-VCH, Weinheim, **2010.**
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