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Preparation, Determination and Characterisation of Gold Nanoparticles Using Flow Injection Techniques

Preparación, determinación y caracterización de nanopartículas de oro usando técnicas de inyección de flujo

Mahmood Mohammed Ali [1], Ahmed Mishaal Mohammed [1, a], Firas Fadhel Ali [2]
[1] Department of Chemistry, College of Science, University Of Anbar, Ramadi, Iraq.
[2] Department of Chemistry, College of Education for women, University of Anbar, Ramadi, Iraq.
[a]Email : Sc.dr.ahmed m.mohammed @uoanbar.edu.iq

ABSTRACT/ This study involves the design of a low-cost flow injection system and the application of a stopped-flow injection technique for preparing a gold nanoparticle (AuNP) solution through the reaction of chloroauric acid with the solution of the citrate. In this solution, the AuNPs were formed and provide good absorption at wavelengths ranging from 510 to 530 nm. The properties of the results prepared were studied by the following measurements: atomic force microscopy, UV spectroscopy, scanning electron microscopy and X-ray diffraction. The method includes designing an optimal system and examining the optimum conditions of preparation (i.e. reactor length, time to stop the reaction and initial pumping speed), as well as the factors influencing the forms, sizes and poly dispersity on the basis of the Turkevich method for preparing AuNPs. These factors include temperature, Au^{3+} concentration, citrate concentration, initial heating, reaction time and the order of the addition of reactants. The dispersion coefficient was calculated for concentrations of (20 and 40) mg/L of gold ions; the values were 1.85 and 1.73, respectively which were considered within the limited dispersion values. Keywords: stopped-flow, AuNPs, Dead volume, interfering ions, Reproducibility. RESUMEN/ Este estudio implica el diseño de un sistema de inyección de flujo de bajo costo y la aplicación de una técnica de inyección de flujo detenido para preparar una solución de nanopartículas de oro (AuNP) a través de la reacción del ácido cloroaúrico con la solución del citrato. En esta solución, se formaron los AuNP y proporcionan una buena absorción a longitudes de onda que varían de 510 a 530 nm. Las propiedades de los resultados preparados se estudiaron mediante las siguientes mediciones: microscopía de fuerza atómica, espectroscopía UV, microscopía electrónica de barrido y difracción de rayos X. El método incluye diseñar un sistema óptimo y examinar las condiciones óptimas de preparación (es decir, la longitud del reactor, el tiempo para detener la reacción y la velocidad de bombeo inicial), así como los factores que influyen en las formas, los tamaños y la dispersión polivinílica en función del método de Turkevich. para preparar AuNPs. Estos factores incluyen temperatura, concentración de Au^{3+}, concentración de citrato, calentamiento inicial, tiempo de reacción y el orden de adición de los reactivos. El coeficiente de dispersión se calculó para concentraciones de (20 y 40) mg / L de iones de oro; los valores fueron 1.85 y 1.73, respectivamente, que se consideraron dentro de los valores de dispersión limitados. Palabras clave: flujo detenido, AuNP, volumen muerto, iones interferentes, reproducibilidad.

Introduction

The FIA technique is based on the injection of a liquid sample into a continuously moving carrier solution (1). The injected sample is an area that moves to the mixing coil and then produces a product towards the detector that continuously records the absorbance, electrode voltage or any other physical factor that changes as a result of the flow cell (2, 3). The simplest device for flow injection analysis is similar to High Performance Liquid Chromatography (HPLC). The method of inserting the sample, analytical current and valves (4) and the mixing conditions are

similar. Flow injection analysis has several features (5), including higher efficiency and productivity compared with the one-batch method; high modelling rate of 50–300 samples per hour, which reduces the analysis time; and low detection limit (6).

Several types of flow injection technique are available (7). Sequential injection analysis, which is characterized as a single-channel system, is considered the second generation of FIA technology. In reverse flow injection (8), the reagent solution is injected into the sample solution as the samples become the carriers. The FIA system can be linked with fluorescence (9), chemiluminescence (CL) (10) and luminescence (11).

The size of nanoparticles ranges from (1 to 100) nm. Such particles are usually larger than atoms and molecules but are smaller than solid masses. Nanotechnology is defined as a small object acting as a whole part in terms of chemical and physical properties.

In the top–bottom methods, the size of the large particles is reduced to nanoscale via high-power processes, such as ball grinding (12) or laser abrasion (13). In a bottom–up path, nanoparticles are created by the nucleation of atoms and molecules that grow into required nanoparticles. Chemical vapour deposition (14) is an example of such techniques.

The flow injection technique is used to prepare nanoparticles after linking it with other techniques. Nanoparticles can also be used as catalysts within a flow injection system (15, 16). Salazar-Alvarez studied the preparation of iron oxide with a small particle distribution. Li Shifeng used gold nanoparticles (AuNPs) in promoting the chemiluminescence of luminol-$NaIO_4$ or luminol-H_2O_2 to estimate compounds, such as polyphenols (17). Norouzi used Pt-nanoparticles and Carbon- Nanotubes within FIA system to stimulated electron transport and enhanced the sensitivity of detection to measure the concentration of Glutamate (18).

The aim of the research is to develop a simple and sensitive spectral method for the preparation and determination of AuNPs. The research includes design a new flow injection system to prepare and study of the optimal conditions for the preparation of gold nanoparticles using the innovative system and study the effect of determinants of the Turkevich method and evaluation of the dispersion coefficient and dead volume for the system.

Materials and methods

-Chemical solutions

The stock solution was prepared by dissolving 1 g of $HAuCl_4 \cdot 3H_2O$ in 100 mL of distilled water to prepare 25 mmol/L as a stock solution. The required concentrations were prepared by performing sequential dilution operations. Trisodium citrate (2 g) was dissolved in 200 mL distilled water to produce a concentration of 34 mmol/L.

The standard method for AuNPs preparation involves heating 50 mL of $HAuCl_4 \cdot 3H_2O$ solution, depending on the required concentrations, for 10 min using a magnetic hot plate at 95 °C. Then, 5 mL of 1% trisodium citrate solution was added to the preheated $HAuCl_4 \cdot 3H_2O$ solution. Continuous heating and stirring was performed for 20 min until the solution begins to turn red. Then, the reaction was stopped, and the resulting solution was cooled at room temperature and then kept in the refrigerator at 5 °C.

-FIA system design

The nature of the reaction requires using a stopped-flow technique to provide sufficient time to complete the reaction between the Au^{3+} ions and the trisodium citrate. Using this technique depends on stopping the flow to increase the duration of the residence for increased sensitivity of the reaction. The optimum design for AuNP preparation is to use chloroauric acid as a carrier stream and inject citrate into the injection valve, where a better signal can be obtained compared with the inverse method (that is, according to the parameters of the device used). Figure 1 presents the FIA system design.

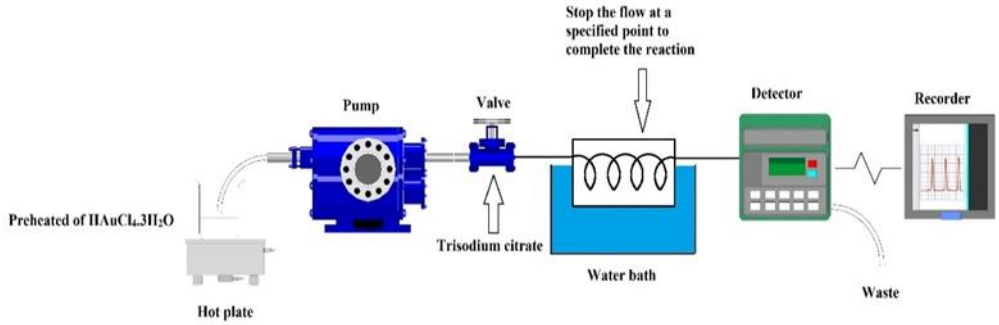


Figure 1: The optimum design for gold nanoparticles preparation

Results and discussion

Determination of AuNP wavelength

The surface plasmon resonance phenomenon is responsible for the colour of the AuNPs formed. AuNPs are known to have absorption peaks between 510 nm and 530 nm, as shown in Figure 2.

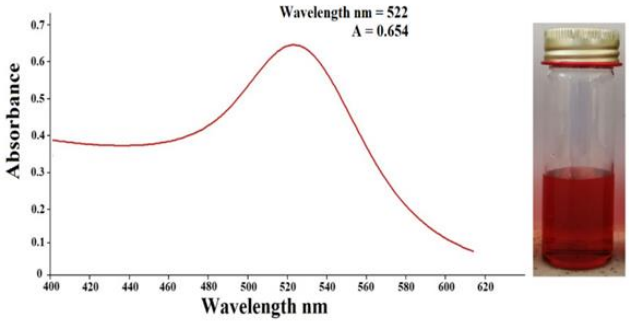


Figure 2: UV-Vis spectroscopy for AuNPs

X-ray diffraction (XRD)

Figure 3 shows the XRD patterns of the sample compared with those of the ICDD card no. 00-004-0784, which is the standard reference of AuNPs. Diffraction peaks indexed to (111), (200), (220), and (311) planes were observed, which confirmed that the face-centred cubic structure of the AuNPs showed peaks at 2θ = 38.1°, 44.3°, 64.5° and 77.7°, respectively, in all samples (Figure 3).

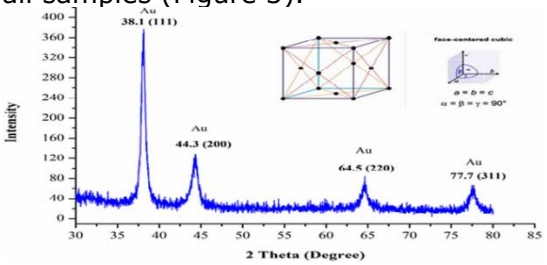
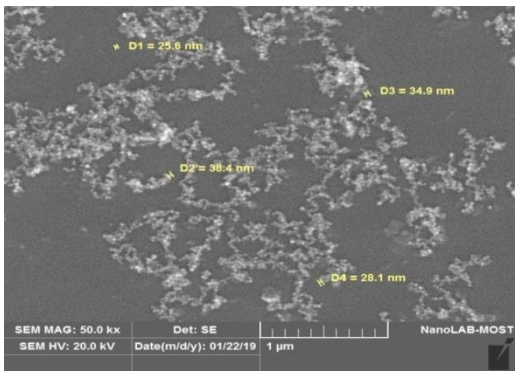
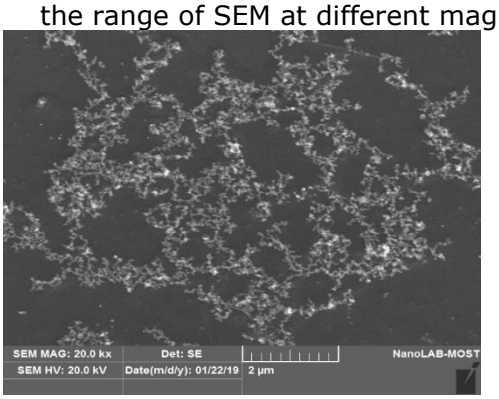


Figure **3.** X-ray diffraction pattern of AuNPs compared to standard Au (ICDD no 00-004-0784).

Scanning electron microscopy (SEM) measurements

Figure 4 shows the SEM micrographs, specifically for the morphological characteristic and structures of the particles and the measured grain size of the samples. The morphology of the AuNP samples shows uniform nanostructures with an average size in the range of SEM at different magnifications.





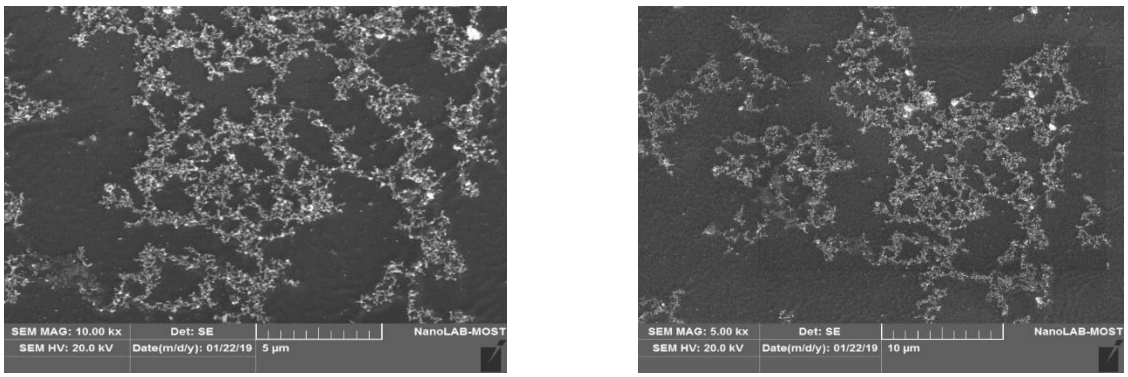


Figure 4. SEM micrograph of AuNPs in different magnification

Atomic force microscopy (AFM) measurements

AFM measurement was conducted to examine the morphological characteristics of AuNPs. Practical determination was performed on the basis of the size information (i.e. length, width and height) and other properties (e.g. morphological characteristics and surface texture).

Figure 5 shows the two- and three-dimensional views of the surface structure of AuNPs. From the figure, the AuNPs had a small particle size distribution with a diameter of 53.73 nm. All AFM analysis results were in agreement with the data obtained by XRD.

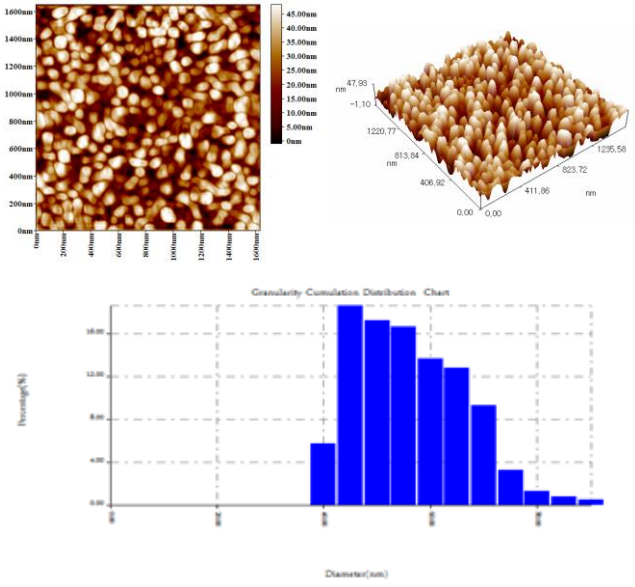


Figure 5: AFM of 2-dimensional and 3-dimensional of AuNPs the average distribution of diameter 53.73 nm

Preparation conditions

The factors affecting the preparation of AuNPs are divided into two groups, First group of factors related to the design of the device, and the second group that affect the shapes and sizes of nanoparticles according to the Turkevich method. These factors include concentration of gold ions, effect of citrate, temperature, reaction time and inverse method.

The factors related to the design of device include the lengths of reaction coil, pumping speeds and the time to stop the flow

The lengths of reaction coils used were 0.5 m and 1 m. The best response was obtained with 0.5 m as opposed to another length. The other parameters were (temperature = 90 °C, time of reaction = 30 min, the concentration of citrate =38 mM, amount of citrate= 20 µL and the concentration of Au^{3+}= 20 mg/L) (Figure 6).

Different pumping speeds of 1000, 700 and 500 µL/min were used. Pumping speeds of 700 µL/min and 500 µL/min had close outcomes and recorded the highest peaks in contrast to the 1000 µL/min speed. The other parameters were (reaction coil length = 0.5 m, conc. of Au^{3+} = 20 mg/L, conc. of citrate = 38 mM, amount of citrate = 20 µL and the time to stop the flow = 5 s) (Figure 7).

Different times were used to calculate the appropriate time to stop the flow inside the reaction coil (5, 8 and 11 s). The 5 s period showed the best response and the highest peak. The other parameters were (reaction coil length = 0.5 m, conc. of Au^{3+} = 20 mg/L, conc. of citrate = 38 mM, amount of citrate = 20 µL and Pumping speed = 700 µL /min) (Figure 8).

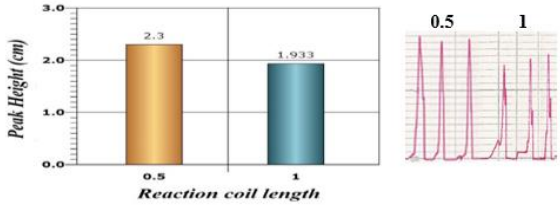


Figure 6: The effect of reaction coil length

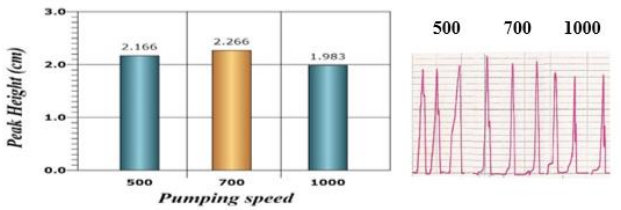


Figure 7: The effect of pumping speed

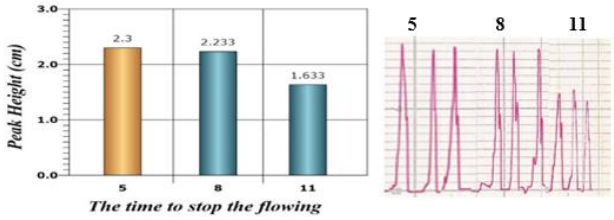


Figure 8: The effect of "time to stop the flow"

The factors affecting on the shapes and sizes of the nanoparticles formed according to the Turkevich method include the concentration of gold ions, effect of citrate, temperature, reaction time , initial heating and the order of the addition of reactants.

The response of the flow injection device to changes in the concentration of gold ions was studied by increasing the concentration and measuring the height of the peaks obtained. The other parameters were (temperature = 90 ^{o}C, reaction time = 30 min, conc. of citrate = 38 mM, amount of citrate = 20 µL, reaction coil length = 0.5 m and Pumping speed = 700 µL /min) (Figure 9).

Different times were used to study the effect of the time of stopping or the reaction time on the formation of AuNPs and examine the response of the flow injection system with the increasing reaction time. The signal obtained increased over time. The other parameters were (temperature 90 ^{o}C, conc. of Au^{3+} = 20 mg/L, conc. of citrate = 38 mM, reaction coil length = 0.5 m and Pumping speed = 700 µL /min) (Figure 10).

By using different temperatures for the synthesis of AuNPs, we studied the response of the flow injection system with temperature changes. The other parameters were (reaction time = 30 min, conc. of Au^{3+} = 40 mg/L, reaction coil length = 0.5 m and Pumping speed = 700 µL /min) (Figure 11).

The effect of the initial heating of the carrier stream on the peak height in the flow injection system was investigated. The other parameters were (reaction time = 30 min, conc. of Au^{3+} = 20 mg/L, reaction coil length = 0.5 m and Pumping speed = 700 µL /min) (Figure 12).

The effect of using different volumes of citrate was negligible. The final size stayed nearly the same without any change by using increased citrate concentrations. The effect of citrate on the final size became evident with high or low concentrations (19).

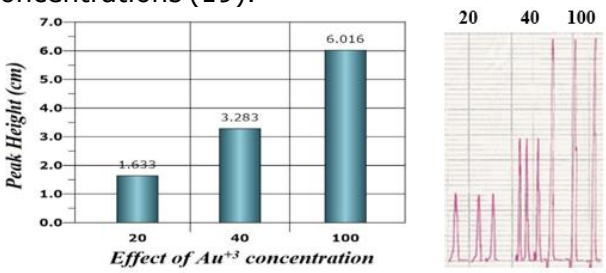


Figure 9: The effect of Au^{3+} concentration (20, 40,100) mg/L

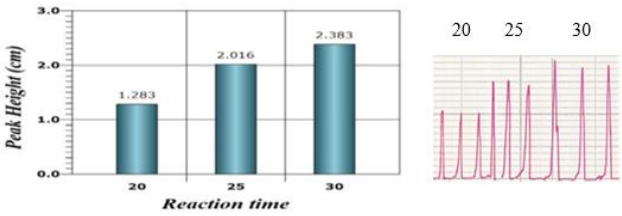


Figure 10: The effect of reaction time (20, 25, 30) min

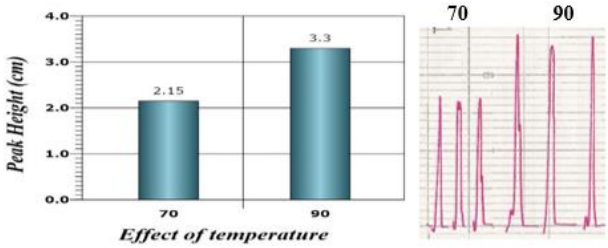


Figure 11: The effect of temperature (70, 90) ^{o}C

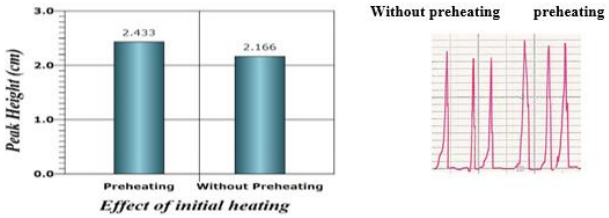


Figure 12: The effect of preheating the carrier stream

The dead volume was measured via experiments as follows. The First experiment by using distilled water as a carrier stream instead of chloroauric acid, and trisodium citrate was injected in the injection valve. After the experiment, we did not obtain a response from the recorder.

The Second experiment includes injecting the distilled water into the injection valve, and

using chloroauric acid as a carrier stream (optimum conditions were applied). We did not obtain a response from the recorder as well.
These experiments show that the dead volume in the system is zero. The quality of the system and the validity of the results are shown in Figure 13.

Figure 13: Study the dead volume in the flow injection system

A- Distilled water injected into the injection valve, with chloroauric acid as a carrier stream
B- Distilled water as a carrier stream with the injection of citrate in the injection valve.

The degree of dilution can be expressed by the dispersion coefficient D, as shown as equation no. (1):

$D = H^0 / H_{MAX}$ ..... (1)

Where H^0 is the height of the peak without dilution, and H_{MAX} is the height of the peak with dilution

The dispersion was measured by using two experiments. In the first experiment, the AuNPs solution was passed as a carrier stream through the system to obtain a response represented by H^0. For the second experiment, citrate was injected into the injection valve with chloroauric acid as a carrier stream to obtain a response that represented H_{MAX}. The dispersion coefficients were calculated for concentrations of (20 and 40) mg/L (Figure 14)

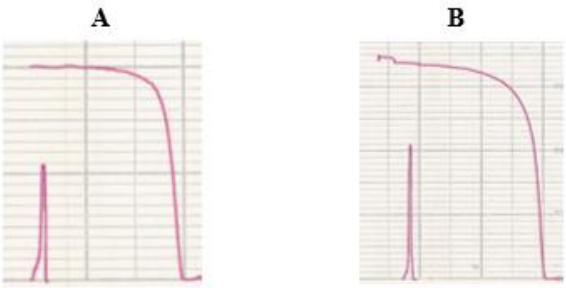


Figure 14: Calculation of dispersion coefficient **A-** For 20 mg/L (D = 2 / 1.08 = 1.85) **B-** For 40 mg/L (D = 3.65/ 2.1 = 1.73)

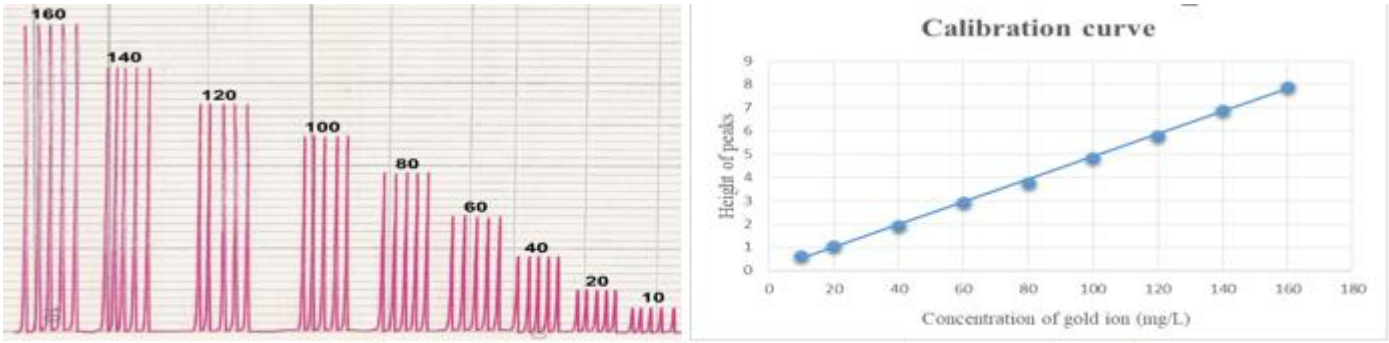
Determination of AuNPs

A series of AuNP solutions were prepared by using the batch method with Au^{3+} concentration ranging from 5 mg /L to 200 mg /L, citrate concentration of 38 mM, and temperature of 95 °C (standard methods). The following results were studied

At 30 °C, pumping speed of 1500 µL/min, and 20 µL of the injected sample, the calibration curve was calculated. The linearity of the results was found 10–160 mg /L, and the detection limit was 5 mg /L (Table 1 and Fig 15).

Table 1: The values of calibration curve

Conc. of Au^{3+}(mg/L)	Peak Height (cm)					Mean	S.D	R.S.D%
10	0.63	0.63	0.63	0.63	0.63	0.63	0	0
20	1.07	1.07	1.05	1.05	1.05	1.058	0.01	0.945
40	1.93	1.93	1.96	1.93	1.93	1.936	0.013	0.671
60	2.95	2.96	2.93	2.93	2.95	2.944	0.013	0.441
80	3.8	3.78	3.8	3.78	3.8	3.792	0.01	0.026
100	4.849	4.85	4.848	4.848	4.85	4.849	0.001	0.02
120	5.803	5.805	5.8	5.8	5.8	5.802	0.002	0.034
140	6.897	6.9	6.9	6.9	6.9	6.899	0.001	0.014
160	7.898	7.896	7.9	7.9	7.896	7.898	0.002	0.025



Slope	y-intercept	R^2	r	Equation of chart
0.0485	0.0261	0.9985	0.9992	y = 0.0485X + 0.0261

Figure 15: Calibration curve of flow injection system

Calibration curve obtained was used to estimate the concentration of Au^{3+}. To check the quality of the proposed method and the efficiency in the estimation of the gold ions, the results of AuNPs solutions obtaind from flow injection analysis (FIA) were compared with those from the atomic absorption spectroscopy method (AAS) (Table 2).

Table 2: Estimate Au^{3+} in various samples

Samples	Concentration of Au^{3+}(AAS) (mg/L)	Concentration of Au^{3+}(FIA) (mg/L)	Rec %	Relative Error %
Aqueous Solutions	31.1	30.2	97	2.9
	52.05	50.1	96	3.7
Gold Jewellery	11.2	9.73	87	13
	17.02	14.4	85	15

Effects of interfering ions

The effect of some positive ions on the synthesis of the AuNP solution was studied. Some ions, such as K^{1+} and Ca^{2+}, did not cause any interference. Other ions caused positive or negative interference according to the concentrations added (Table 3).

Table 3: The effect of interfering ions

Ions	Concentration of Au^{3+} (mg/L)	Concentration of interference ions (mg/l)	The amount of interference (cm)	The treatment
K^{1+} ,Ca^{2+}	40	40	0	-----
	40	80	0	
Na^{1+}	40	40	- 0.1	HCl , Reverse osmosis
	40	80	-1	
Zn^{2+}	40	40	- 0.5	Na_2EDTA
	40	80	- 0.3	
Cu^{2+}	40	40	+ 0.2	Na_2EDTA
	40	80	+ 0.1	
Ni^{2+}	40	40	0	tri methylene di nitrile tetra acetic acid (TMDTA)
	40	80	- 0.3	

Cd^{2+}	**40**	**40**	**0**	**K_3EDTA**
	40	**80**	**- 0.2**	
Fe^{3+}	**40**	**40**	**+ 0.81**	**nitrilo tris (methylene) tri phosphonic acid (NTTA)**
	40	**80**	**+1.7**	
Mn^{2+}	**40**	**40**	**- 1.65**	**poly acrylic acid (PAA)**
	40	**80**	**- 0.78**	

Conclusions

A new flow injection system was developed, and the stopped-flow injection technique was used. This technique was utilised to prepare AuNPs. The effects of the factors affecting the nanoparticle formation was also studied. This system was characterised by high repetition, wide linear range, low dispersion ratio, and consumption of small volumes of reagents and the carrier solution. A new technique was also developed for the estimation of gold ions through the flow injection system and achieved a 97% recovery rate and relative error of 2.9.

References

1- Al-Zaydany, F. F. A.; Taha, D. N., "Determination of Cerium (IV) by Continuous flow injection and sequential flow injection." Journal of Babylon University/Pure and Applied Sciences, No. (1)/ Vol. (22), 120-131 (2013).
2- Trojanowicz, M., and Kołacińska, K. Recent advances in flow injection analysis. Analyst, Vol. 141(7), 2085-2139. (2016).
3- Gary D. Christian, "Analytical Chemistry", 6th ed, John Willey & sons Ltd, .665, (2004).
4- Leamsomrong, K., Suttajit, M., and Chantiratikul, P." Flow injection analysis system for the determination of total phenolic compounds by using Folin-Ciocalteu assay". ***Asian J Appl. Sci***., Vol.2, 184-190 (**2009**).
5- Gonzalez, P., Knochen, M., Sasaki, M. K., and Zagatto, E. A. "Pulsed flows in flow analysis: potentialities, limitations and applications". ***Talanta***, Vol. 143, 419-430, (2015)
6- Han, S. "Chemiluminescence determination of indole derivatives in human body fluids and soil by flow injection analysis using potassium permanganate". ***Microchimica Acta***, Vol. 168(1-2), 169-175. (2010).
7- Farhood, A. S., Ali, L. A. M., and Ali, F. F. "Determination of aniline blue dye by flow injection analysis with home made valve". ***Oriental Journal of Chemistry***, Vol. 33(2), 944-950 (2017).
8- Trojanowicz, M., and Kaniewska, M. Flow methods in chiral analysis. ***Analytica chimica acta***, Vol. 801, 59-69.(2013)
9- Ge, S., Yan, M., Cheng, X., Zhang, C., Yu, J., Zhao, P., and Gao, W. "On-line molecular imprinted solid-phase extraction flow-injection fluorescence sensor for determination of florfenicol in animal tissues". ***Journal of pharmaceutical and biomedical analysis***, Vol. 52(4), 615-619. (2010).
10- Zeng, H. J., Yang, R., Wang, Q. W., Li, J. J., and Qu, L. B. "Determination of melamine by flow injection analysis based on chemiluminescence system". ***Food chemistry***, Vol.127 (2), 842-846. (2011).
11- Navarrro, M. V., Payán, M. R., López, M. A. B., Fernández-Torres, R., and Mochón, M. C. "Rapid flow injection method for the determination of sulfite in wine using the permanganate-luminol luminescence system", ***Talanta***, Vol.82 (5), 2003-2006 (2010).
12- Russo, L., Colangelo, F., Cioffi, R., Rea, I., and Stefano, L. D. "A mechanochemical approach to porous silicon nanoparticles fabrication". ***Materials***, Vol. 4(6), 1023-1033. (2011).
13- Wang, X., Qian, H., Si, P. Z., Yang, Y., Choi, C. J., Park, J., and Chung, K.. "Structure and magnetic properties of MnBi nanoparticles prepared by laser ablation and arc-discharge method", ***IEEE Transactions on Magnetics***, Vol.54 (11), 1-5 (2018).
14- Athanassiou, E. K., Grass, R. N., and Stark, W. J. "Chemical aerosol engineering as a novel tool for material science: from oxides to salt and metal nanoparticles". ***Aerosol Science and Technology***, Vol. 44(2), 161-172 (**2010**).
15- Teerasong, S., Sonsa-Ard, T., Vimolkanjana, C., Choengchan, N., Chompoosor, A., and Nacapricha, D.

"Colorimetric sensor using silver nanoparticles for determination of hydrogen peroxide based on a flow injection system". ***Journal of Nanoelectronics and Optoelectronics***, Vol. 8(5), 446-449. (2013).

16- Peng, M., Li, Z. A., Hou, X., and Zheng, C. "In-atomizer atom trapping on gold nanoparticles for sensitive determination of mercury by flow injection cold vapor generation atomic absorption spectrometry". ***Journal of Analytical Atomic Spectrometry***, Vol. 29(2), 367-373. (2014).

17- Li, S., Tao, S., Wang, F., Hong, J., and Wei, X. "Chemiluminescence reactions of luminol system catalyzed by nanoparticles of a gold/silver alloy". ***Micro chimica Acta***, Vol. 169(1-2), 73-78 (2010).

18- Norouzi, P., Faridbod, F., Rashedi, H., and Ganjali, M. R. "Flow injection glutamate biosensor based on carbon nanotubes and Pt-nanoparticles using FFT continuous cyclic voltammetry". ***Int. J. Electrochem. Sci***, Vol. 5, 1713. (2010).

19- Li, C.; Li, D.; Wan, G.; Xu, J.; and Hou, W. "Facile synthesis of concentrated gold nanoparticles with low size-distribution in water: Temperature and pH controls". ***Nanoscale Res. Lett***., Vol. 6, 440-447 (2011).