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Synthesis and Characterization of Gold Nanoparticles

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***ABSTRACT*:-**In this paper, Gold Nanoparticles (GNPs) has been successfully prepared by chemical reduction method (TERKEWISH method) using Sodium Citrate as reducing agent and by Green method using Fructose as reducing agent. The synthesized gold colloidal solution is characterized by using ZETA POTENTIAOMETER, FTIR and UV-VIS spectroscopy. Results of zeta shows that GNPs with sodium citrate have particle size of 119.5 nm (diameter) and have incipient stability. GNPs made with green method using fructose have particle size 50 nm (diameter) and have moderate stability. Results of FTIR are in good agreement to that has been explained in literature. Results of UV- VIS shows that GNPs with sodium citrate gives peak at 526 nm and GNPs made with green method using fructose gives peak at 520 nm, these results match with literature reviews.

Keywords: *Nanotechnology, gold nanoparticles, spectroscopy, zeta potentiometer*.

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1. INTRODUCTION

Chemistry of gold colloids began from the nineteenth century, when Michael Faraday performed his well known experiments for gold colloids generation. His experiments yield deep red gold sols by reduction of tetrachloroaurate with the help of white phosphorus [1]. At the start of the 20th century, Wilhelm Ostwald contributed positively to the supplementary progress of colloid science. He pointed out that in the nm range, the properties of metal particles are mainly defined by surface atoms and he reasoned that these nanoparticles, called colloids, should show novel properties with respect to bulk particles. The trimness of gold to the nanometer range has dramatic consequences for its physical and chemical properties [2]. These consequences are also well-founded for other metals however, Gold is an outstanding example.

In the literature, various metal nanoparticles have been reported. But the promising candidate is gold because of its outstanding surface properties [3]. These surface properties can be used in biotechnological, optical and electrochemical applications. There are various advantages of the gold nanoparticles like non-toxicity, strong scattering length, bio-conjugation and long-term stability. These features are fundamental for a secure and responsive biosensing policy.

Gold nanoparticles (GNPs) are the mostwell-suited nanomaterial for groundwork of engineered nanoplatforms in smart sensing devices. Surface Plasmon resonance property of GNP makes them useful nanomaterial in various fields like bioimaging, biomedical therapeutics and biodiagnostic tools [4]. GNPs are also called as gold colloids. There are huge global demands of gold colloids because of their significant requirement in many industrial and commercial applications. Biomolecule GNPs are used in the medicine and in cosmetic products as these have anti-aging components for skin protection [5]. GNPs are used for doing permanent coloration of wool or cotton fibres. These are also used for novel coatings and paintings. These are also used as catalysts [6]. Due to all above advantages, more attention should be paid on effective synthesis methods to match the enlarging demand of GNPs.

In this paper, Gold Nanoparticles has been successfully prepared by chemical reduction method (TERKEWISH method) using Sodium Citrate and by Green method using Fructose as reducing agent. The synthesized gold colloidal solution is characterized by using ZETA POTENTIAOMETER, FTIR and UV-VIS spectroscopy. Results of zeta shows that GNPs with sodium citrate have particle size of 119.5 nm (diameter) and have incipient stability. GNPs made with green method using fructose have particle size 50 nm (diameter) and have moderate stability. Results of FTIR are in good agreement to that has been explained in literature. Results OF UV- VIS shows that GNPs with sodium citrate gives peak at 526 nm and GNPs made with green method using fructose gives peak at 520 nm, these results match with literature reviews.

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2. SYNTHESIS OF GOLD NANOPARTICLES

Gold nanoparticles are synthesized by liquid chemical method and green synthesis method [7-9]. GNPs are produced by reducing chloroauric acid ($HAuCl_4$) in a liquid. After dissolving $HAuCl_4$, a reducing agent was added in the solution with constant stirring. After reaction with reducing agent, gold ions Au^{3+} reduced to neutral gold atoms and gold slowly starts to precipitate in the form of sub-nanometer particles. For formation of uniform gold nanoparticlels, fast stirring of solution was done.

2.1 MATERIAL USED

The chemicals used in this study were mostly dried and were prepared according to requirements. The materials used in synthesis of GNPs include auric-chloride ($HAuCl_4$), trisodium citrate from Sigma, fructose and mili poure water.

2.2 CLEANING OF GLASSWARE AND MAGNETIC STIRRER

All the glassware like beakers, pipettes, condenser, three necked flasks (250 or 150 mL) and magnetic beads were first washed with millipore water. Then glassware and magnetic beads were washed with liquid detergent. After detergent washing, glasswares were washed with normal tap water. Then all materials were dipped in aquaregia (3:1 mixture of concentrated HCl and HNO_3 respectively) for at least an hour. Aqua regia should be prepared very carefully wearing goggles and gloves in a fume hood. Aqua regia should be always freshly prepared. Aqua regia should never be stored in a closed bottle otherwise it may explode. After aqua regia, glassware were washed with copious amount of double distilled water and then rinsed with millipore water in sequence.

2.3 METHODS

In the literature, synthesis of nanoparticles was done by various methods. Here we use chemical method [10-11] using sodium citrate as a reducing agent and green method [12] by using fructose as a reducing agent.

2.3.1 CHEMICAL REDUCTION METHOD

Gold nanoparticles were synthesized by citrate reduction method originally introduced by Turkevitch [13-14] with slight modifications described by Liu and Lu [15] in aqueous phase using trisodium citrate and other agents for reduction. This method was carried out in following steps.

First of all gold stock solution was made by mixing 0.03g of gold salt ($HAuCl_4$) with 100 mL of Millipore water as shown in fig.1.

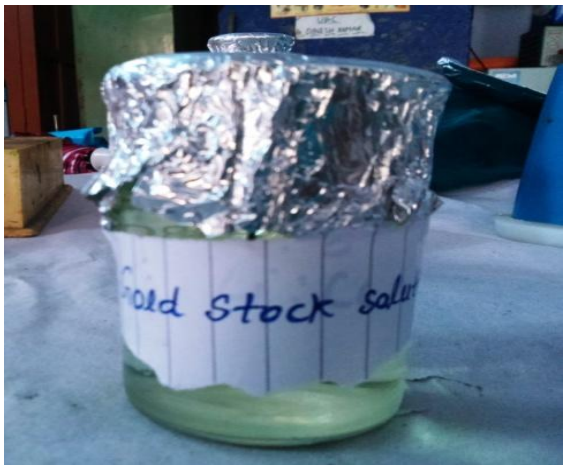

Fig.1: Gold stock solution

Then 10 ml of gold stock solution was added to a three conical flask, After putting magnetic bead in the flask, glass condenser was connected to central neck of the flask and stopper on the side neck flask and whole assembly was placed on the magnetic stirrer for 20 min at 60°C temperature as shown in fig.2.

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Fig.2: Whole set up placed on magnetic stirrer

With continuous stirring gold chloride solution was heated upto boiling. Then trisodium citrate solution shown in fig.3, which was made by mixing of 1g trisodium citrate with 100 ml of milipoure water, was added drop wise.

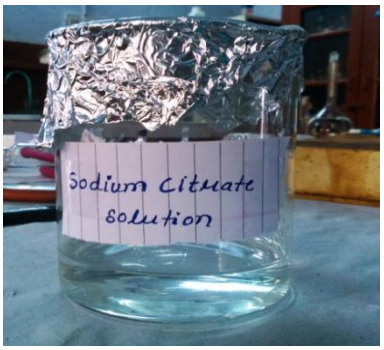

Fig.3: Trisodium citrate solution

Then the boiling was further continued with continuous stirring. Gradual change in the colour of the gold chloride solution from pale yellow to deep red and one minute after addition of trisodium citrate dihydrate solution indicates the formation of colloidal GNPs shown in fig.4. The mixture was allowed to reflux for another 20 min. Heating was turned off and the mixture was allowed to cool upto 23-25ºC at room temperature with continuous stirring.

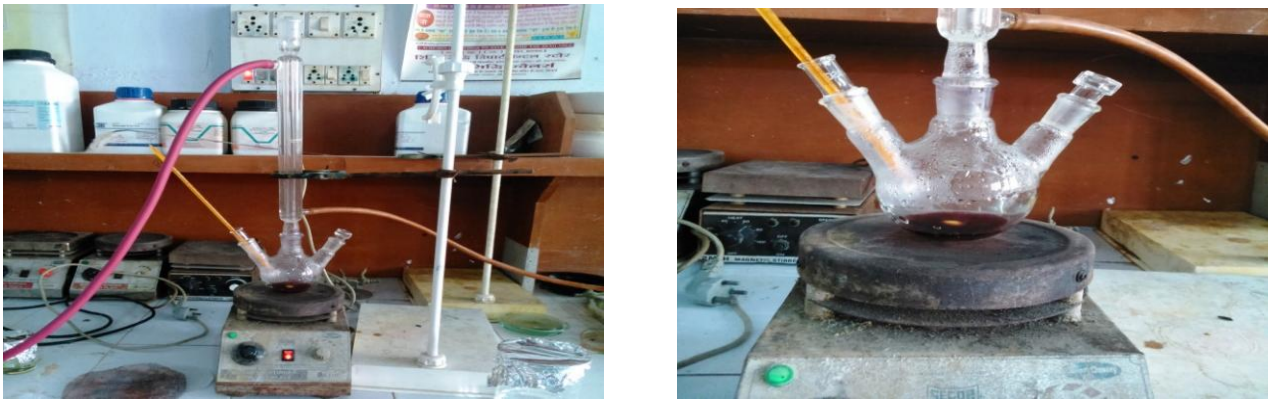

Fig.4: Formation of gold nanoparticles

Synthesized gold nanoparticles were collected in a clean amber-coloured glass container (washed with aquaregia/acetone) as shown in fig.5 and stored at 4ºC.

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Fig.5: Formed gold nanoparticles using chemical reduction method

2.3.2 GREEN SYNTHESIS METHOD

Due to toxic chemicals, non eco friendly and various other deleterious effects of traditional chemical and physical methods that are being employed for the generation of gold nanoparticles, focus has now being targeted towards "green chemistry" for synthesis of gold nanoparticles [16]. In this method, gold nanoparticles were made by using fructose as a reducing agent. This method proceeds in the following steps.

Fructose solution was made by mixing 0.2 g of fructose with 3.9 mL of Millipore water. Then this solution was added to a three conical flask, After putting magnetic bead in the flask, glass condenser was connected to central neck of the flask and stopper on the side neck flask and whole set up was placed on the magnetic stirrer for 10 min at 70-75°C temperature as shown in fig.6.

Fig.6: Whole set up of green synthesis method

Fructose solution was heated upto boiling with continous stirring. When refluxing was started in fructose solution, stopper from the side neck of the flask was removed followed by quick addition of 0.1 ml gold stock solution by using micro pipette with simultaneous stirring and stopper placed back.The boiling was further continued with continuous stirring. Gradual change in the colour of the gold chloride solution from pale yellow to deep red, after addition of gold stock solution indicates the formation of colloidal GNPs as shown in fig.7.

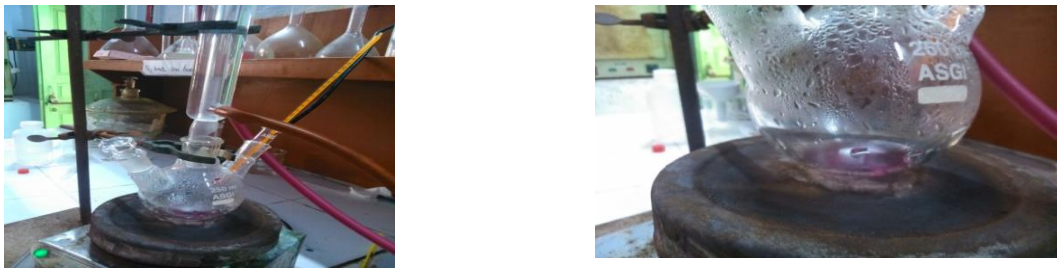

Fig.7: Gold nanoparticles start to form

Heating was turned off and the mixture was allowed to cool upto 23-25ºC at room temperature with continuous stirring. Gold nanoparticles were collected in a clean amber-coloured glass container shown in fig.8 and stored at 4ºC.

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Fig.8: Formed gold nanoparticles using Green synthesis method

3. CHARACTERISATION

Relationship between particle size and colour was observed by transparency and turbidity. Turbid solutions indicate aggregate formation of different sizes [17]. The size, shape and other properties of synthesized gold nanoparticles were characterised by using UV-spectrophotometer [18]. Nanoparticle formations were detected by transparency observations and red wine coloured solutions. By using Zeta-sizer, particle size and size distribution of synthesized gold nanoparticles were found [19]. The synthesized gold nanoparticles were imaged by scanning electron microscope [20].

3.1 UV-VIS SPECTROPHOTOMETRY:

For characterization of gold nanoparticles, there is an important aspect known as spectrophotometry [21]. The synthesized gold colloidal solution is characterized by using ZETA POTENTIAOMETER, FTIR and UV-VIS spectroscopy. In the spectroscopy results, there is a shift of absorption peak towards longer wavelength with increase in particle size. GNPs size distribution range is defined by the absorption spectra width [22]. Generally, a single absorption peak in the visible range between 510-550 nm is displayed by gold nanospheres, because of SPR. GNPs shows intense absorption of visible light at 520 nm, cause for their brilliant red color, and it will be different for different sizes [23]. In the present study, measurement of GNPs absorption was done in single beam spectrophotometer. There are notable absorption maxima at different wavelengths (390-630 nm). Synthesized colloidal gold shows intense absorption at 520 nm. The absorbance at 520 nm was 1.368.

Fig.9: Zeta potentiometer

Related to nanoparticle stability, there is another important parameter known as zeta potential. A more stable dispersion is predicted by large zeta potential [24]. Measurement of the zeta potential, or electrostatic attraction / repulsion, is important to many industries from pharmaceuticals to mineral processing and from water treatment to additives for electronics. The SZ-100 shown in fig. 9 enables fast, reliable and accurate measurement of the zeta potential [25-27].

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To obtain homogeny of size, colloidal gold solution was centrifuged at 8000 rpm for 10 minutes. Counts were taken. The peak mean gives the mean diameter of particle. The graphs were plotted using the means of all peaks mean diameter and the intensity of peak area. Beside size distribution, the zeta potential measurement is also of great importance for characterization. The negative charge was also another important indicator of particle size. Zeta potential measurements at the end of the reduction reaction were negative because of citrate ions. Hence, the nanoparticle size diameters small than 100 nm were obtained in the research. The zeta potentials of the nanoparticles synthesized in the scope of this study was obtained between -4 and -5 mV.

RESULT AND DISCUSSION

1. STRUCTURAL CHARACTERIZATIONS

1.1 STRUCTURAL CHARACTERIZATION OF GNP WITH SODIUM CITRATE

1.1.1. Measurement of size from zeta Potentiometer:-

Fig.10 shows the size distribution of GNP with Sodium citrate using zeta potentiometer outputs mentioned in table 1. The average diameter size of GNP with Sodium Citrate comes out to be 119.5nm, which shows particles made are of large size.

Results

			Size (d.nm):	% Intensity:	St Dev (d.n...
Z-Average (d.nm):	119.5	Peak 1:	170.2	97.5	82.18
PdI:	0.421	Peak 2:	4837	2.5	707.5
Intercept:	0.895	Peak 3:	0.000	0.0	0.000
Result quality :	Refer to quality report				

Table1: Size distribution outputs of GNP with sodium citrate

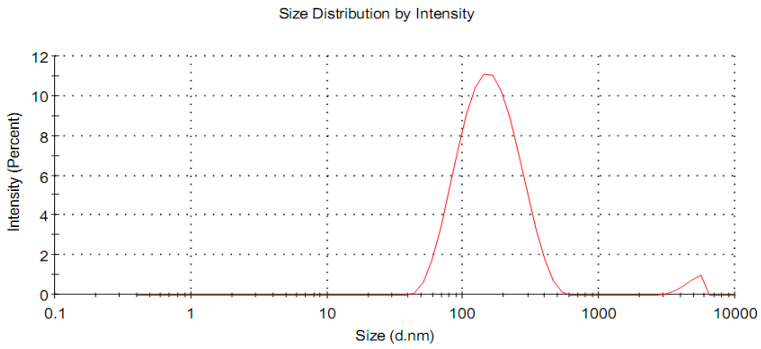

Fig. 10: GNP size distribution by intensity curve with sodium citrate

1.1.2. Zeta Potential Distribution

Fig.11 shows Zeta Potential distribution of GNP with Sodium citrate on the basis of outputs mentioned in table 2. It shows zeta potential of GNP with Sodium Citrate is -19.0. Hence stability of GNP is incipient.

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		Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV): -19.0	Peak 1:	-25.4	73.4	6.81
Zeta Deviation (mV): 13.3	Peak 2:	-0.985	19.6	3.85
Conductivity (mS/cm): 0.307	Peak 3:	8.96	7.0	2.72

Table2: Zeta potential distribution outputs for synthesized GNPs with sodium citrate

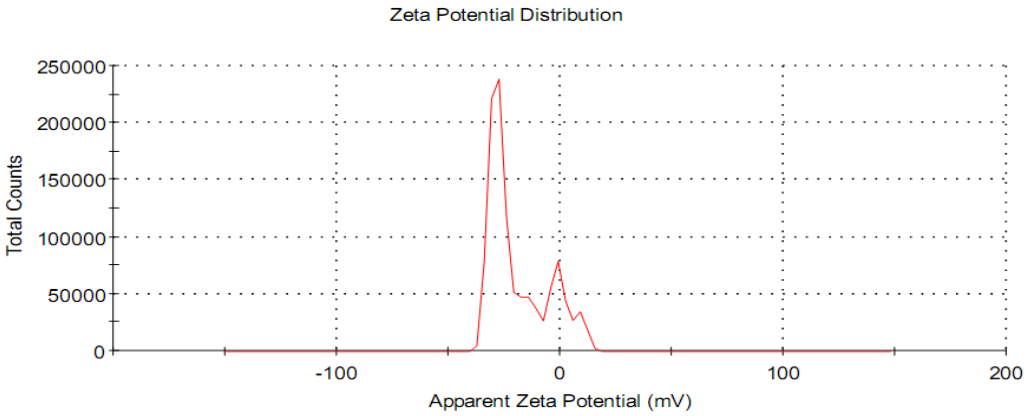

Fig.11: Zeta potential distribution curve of GNPs with sodium citrate

1.2 STRUCTURAL CHARACTERIZATION OF GNP WITH FRUCTOSE

1.2.1. Measure of size from Zeta Potentiometer

Fig.12 shows the size distribution of GNP with fructose using zeta potentiometer outputs given in table3. The average diameter size of GNP with fructose comes out to be 50.04nm, which shows particles made are of normal size.

Table3: Size distribution outputs of GNPs with fructose

		Size (d.nm):	% Intensity:	St Dev (d.n...
Z-Average (d.nm): 50.04	Peak 1:	136.3	83.1	195.0
PdI: 0.559	Peak 2:	4.575	6.5	1.655
Intercept: 0.892	Peak 3:	3422	5.3	1281

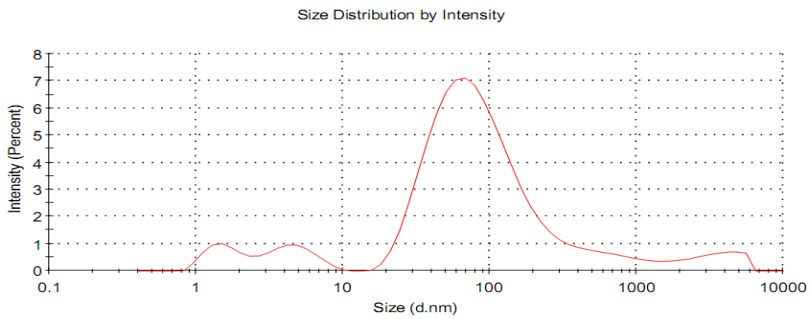

Fig.12: GNP

size distribution by intensity curve with fructose

1.2.2. Zeta Potential Distribution

Fig.13 shows Zeta Potential distribution curve of GNPs with fructose on the basis of outputs given in table4. It shows zeta potential of GNP with fructose is -13.2. Hence stability of GNP is incipient.

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			Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV):	-13.2	Peak 1:	-13.2	100.0	5.92
Zeta Deviation (mV):	5.92	Peak 2:	0.00	0.0	0.00
Conductivity (mS/cm):	0.300	Peak 3:	0.00	0.0	0.00

Table4: Zeta potential distribution outputs for synthesized GNPs with fructose

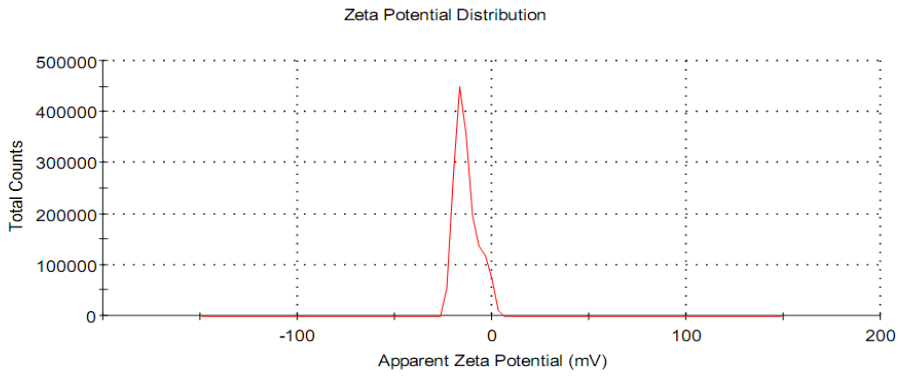

Fig.13: Zeta potential distribution curve of GNPs with fructose

2. FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY

2.1 GNP WITH SODIUM CITRATE

Fig.14 shows the FTIR spectra of GNP with Sodium citrate. FTIR spectrum of the GNP shows six principal absorptions at 3129.94, 3003, 1637, 1474.79, 1231 and 1059.30 cm^{-1}. The peaks at 3129.94 and 3003 cm^{-1} are assigned to C-H ring stretching vibrations. The peaks at 1637 and 1474.79 cm^{-1} correspond to N-H bending (or –C=C- bond) and the symmetric component of the C-C (or C-H) stretching modes. The bands at 1231 and 1059.30 cm^{-1} can be attributed to C-N bonding.

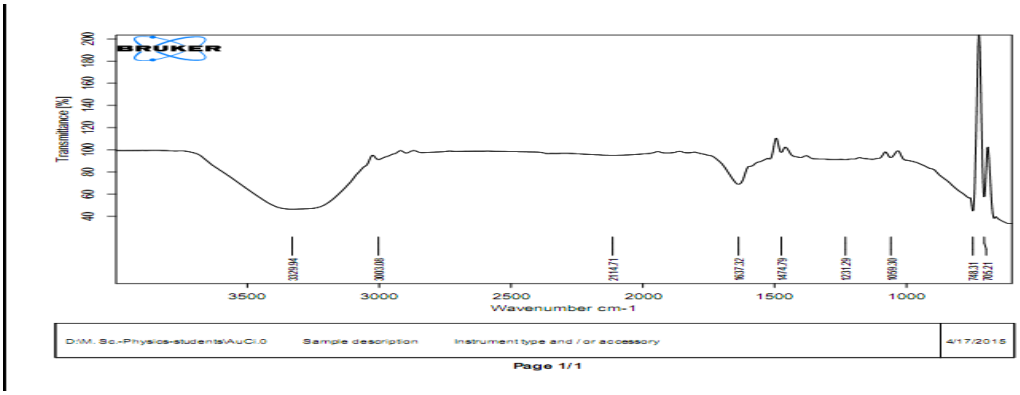

Fig.14: FTIR spectrum of GNPs with sodium citrate

2.2 GNP WITH FRUCTOSE

Fig.15 Shows the FTIR spectra of GNP with Sodium citrate. FTIR spectrum of the GNP shows six principal absorptions at 3326.27, 3002.99, 2108.37, 1637.47, 1474.66 and 1060.50 cm^{-1}. The peaks at 3326.27 and 3002.99 cm^{-1} are assigned to C-H ring

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stretching vibrations. The peaks at 2108.37 and 1637.47 cm^{-1} correspond to –C≡C- stretching and –C=C- stretching. The bands at 1474.74 and 1102.46 cm^{-1} can be attributed to C-H bonding and C-N bonding respectively.

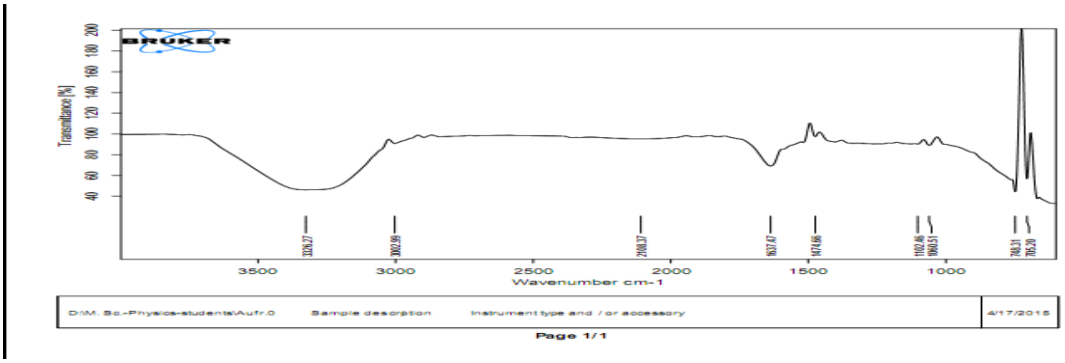

Fig.15: FTIR spectrum of GNPs with fructose

3. OPTICAL CHARACTERIZATION OF THE MATERIALS

3.1 GNP WITH SODIUM CITRATE

The UV-VIS spectra of the GNP synthesized with the use of $AuCl_3$ in H_2O media using Sodium Citrate is shown in Fig.16. The band observed at 300-800 nm for the GNP samples match with literature data. The absorption peak should be observed at 520-530 nm, here we are getting peak at 526 nm.

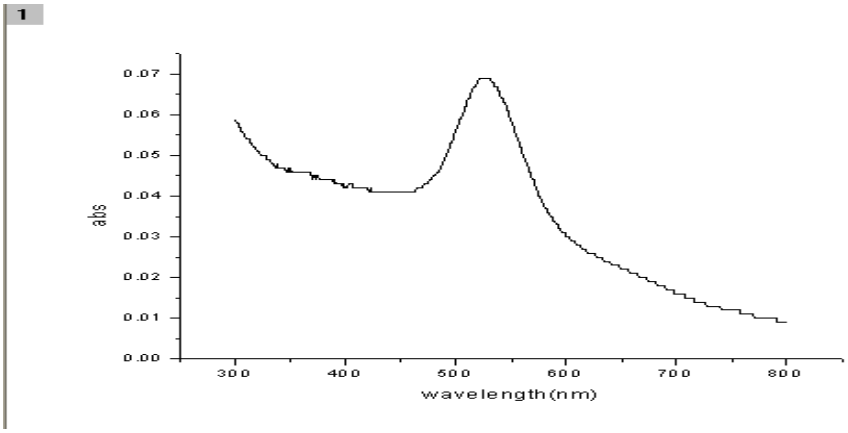

Fig.16: UV-VIS absorption spectra of GNPs with sodium citrate

3.2 GNP WITH FRUCTOSE

The UV-VIS spectra of the GNP synthesized with the use of $AuCl_3$ in H_2O media using fructose is shown in Fig.17. The band observed at 300-800 nm for the GNP samples match with literature data, but we got an additional peak at 731nm. The absorption peak should be observed at 520-530 nm, here we are getting peak at 520 nm.

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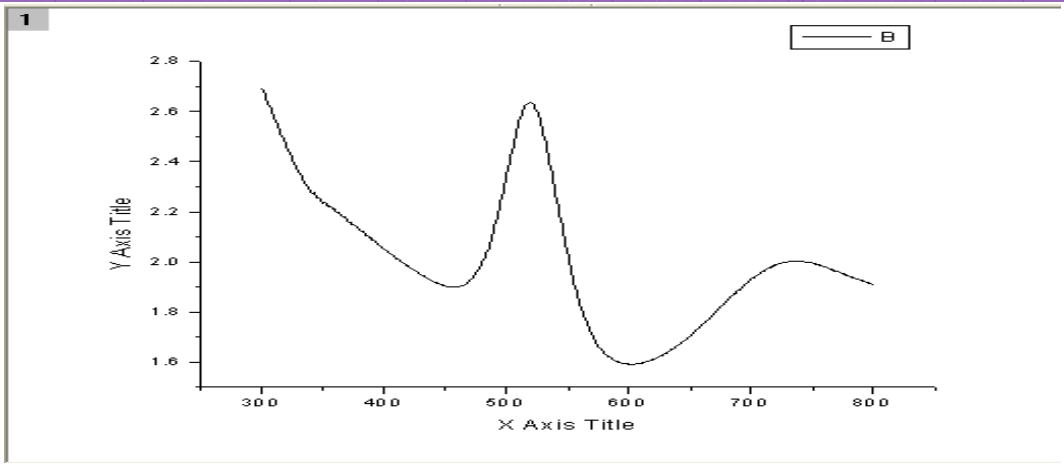

Fig.17: UV-VIS absorption spectra of GNPs with fructose

CONCLUSIONS

Gold Nanoparticles has been successfully prepared by chemical reduction method (TERKEWISH method) using Sodium Citrate and by Green method using Fructose. The synthesized gold colloidal solution is characterized by using ZETA POTENTIAOMETER, FTIR and UV-VIS spectroscopy. Results of zeta shows that GNPs with sodium citrate have particle size of 119.5 nm (diameter) and have incipient stability. GNPs made with green method using fructose have particle size 50 nm (diameter) and have moderate stability. Results of FTIR are in good agreement to that has been explained in literature. Results OF UV- VIS shows that GNPs with sodium citrate gives peak at 526 nm and GNPs made with green method using fructose gives peak at 520 nm, these results match with literature reviews.

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Symbols Used

GNPs – Gold Nanoparticles
H_2O – Water
$HAuCl_4$ – Chloroauric acid
HCl – Hydrogen Chloride
SPR – Surface Plasmon Resonance
FTIR – Fourier Transform Infra Red Spectroscopy
UV-VIS – Ultraviolet –Visible Spectroscopy
Au^{3+} - Gold ions
HNO_3 – Nitric Acid
$AuCl_3$ – Gold Trichloride