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Detection Of 2,4,6-Trinitrotoluene Using A Colorimetric Gold Nanoparticle Air Cassette Filter

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Detection Of 2,4,6-Trinitrotoluene Using A Colorimetric Gold Nanoparticle Air Cassette Filter

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Forensic Science at Virginia Commonwealth University.

by

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ABSTRACT

DETECTION OF 2, 4, 6-TRINITROTOLUENE USING A COLORIMETRIC GOLD NANOPARTICLE AIR CASSETTE FILTER.

By Andrea I. Ferrer Vega, MSFS.

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Major Director: Dr. Sarah J. Seashols-Williams, Graduate Program Director, Department of Forensic Science

Trinitrotoluene (TNT) is an explosive commonly used during military and terrorist activities. Current methods to identify this compound require sampling, transport and analysis at a forensic lab using analytical instrumentation. However, on-site detection is needed to assist efforts to prevent detonation. Gold nanoparticles have been used as sensors throughout the years due to their versatility and surface enhanced Raman scattering properties in the presence of an analyte and low limits of detection. By taking advantage of the Meisenheimer complex that TNT forms in the presence of amines, it is possible to determine its presence at picogram levels. Subsequently, adhering amine functionalized gold nanoparticles to a filter membrane creates a filter-based sensor that allows for testing air samples at the suspected area. In the presence of TNT, the gold nanoparticle containing filter will change color and alert the analyst that TNT is present. The amine functionalized gold nanoparticles were synthesized using a modified Turkevich method. This involved gold chloride, sodium borohydride, cysteamine hydrochloride and ethylenediamine. These nanoparticles were characterized via transmission electron microscopy, dynamic light scattering, and electrophoretic mobility to determine the primary and hydrodynamic particle sizes as well as zeta potential. Reagents and nanoparticles were added to different Whatman filters and the sensitivity of the filters was then tested by adding TNT at different concentrations. In addition, TNT was sampled onto the functionalized filters to determine the detection limits of the filter sensor. A goal for this device could be use in military missions where landmines may be present. With further analysis and optimization of this proposed device, it may be possible to identify the presence of TNT before an explosive detonates and possibly save lives.

ABBREVIATIONS

AuNPs- Gold Nanoparticles

Cys- Cysteamine

DLS- Dynamic Light Scattering

EDA- Ethylenediamine

NPs- Nanoparticles

PDI- Polydispersity Index

PTFE- Polytetrafluoroethylene

TEM- Transmission Electron Microscope

TNT- Trinitrotoluene

CHAPTER 1: INTRODUCTION

In this research project, the goal of this research project was to develop a colorimetric technique based on nanoparticles for the detection of TNT and other nitroaromatic-based explosives using air sampling and testing. This device is expected to be cheaper and faster than the current methodology and is a new procedure that can be employed in crime labs, airports, military bases and government buildings across the nation. In addition, this project allows for the use of nanoparticles in an area where they have been limitedly explored and will open doors to a new field of study in nano-forensics.

TNT is a common explosive that was used in significant amounts in World War I and can be used alone or in mixtures with other materials. This compound is used extensively in agriculture and industrial affairs, as well as military and terrorist activities (1). Public security concerns have promoted the development of procedures to detect TNT as quickly and easily as possible on-site. Trace detection of explosives usually involves the testing of a surface by swabbing a suspected area or collecting debris to then analyze with an array of analytical instrumentation back at the crime laboratory (2). Among the instruments used, the most common ones are liquid chromatography-mass spectrometry (LC-MS), gas chromatography-mass spectrometry (GC-MS), high-performance liquid chromatography (HPLC), and Raman scattering (SERS) (1). These devices usually have low sensitivity and selectivity and can be very time consuming. In addition, the molecular mass of TNT ($C_7H_5N_3O_6$) is almost identical to the molecular mass of nitroglycerine ($C_3H_5N_3O_9$) (TNT, 227.131 g/mol vs. nitroglycerine, 227.0872 g/mol). The nearly same molecular masses may lead to problems when using techniques that rely only on measuring the molecular mass of the species (3). Thus, a novel method that potentially solves these problems and allows for on-site detection of explosives should be investigated.

TNT is considered a high explosive due to its rapid rate of reaction. This is due to the fuel and oxygen source both being contained in the same molecule. The explosive is chemically unstable because the nitro groups are so closely packed that they experience a great deal of strain and hindrance to movement from their neighboring groups, see molecular structure in **Figure 1**. However, it is stable enough to be handled during manufacture and operation and will not explode without a primary detonator. When enough energy is provided, the TNT molecule breaks into nitrogen, carbon monoxide, water, and carbon (4), shown in **Figure 2**.

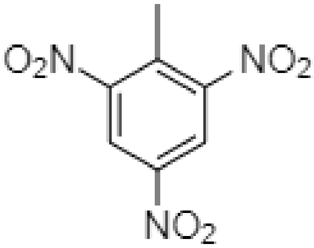

Figure 1. 2,4,6-Trinitrotoluene molecule.

$$2C_7H_5N_3O_{6(s)} \longrightarrow 3N_{2(g)}+7CO_{(g)}+5H_2O_{(g)}+7C_{(s)}$$

Figure 2. 2,4,6-Trinitrotoluene reaction.

In this project, the detection of TNT via aerosol sampling was investigated. Typically, the detonation of 1 gram of TNT produces about 1 liter of gas, which is a 1000-fold increase in volume (5). The vapor pressure of TNT is 4.8 x 10^{-6} torr, and it is considered a medium-vapor-pressure explosive that may be sampled by its vapor or by surface swiping (6). Consequently, these vapors can be extracted from the area of interest and identified using an air sampling technique (7). Usually, the methods employed include an extraction at the crime scene using a filter or a solid phased extraction column (SPE) to gather the vapors. After this, the evidence is sent to the crime laboratory where the explosive identification occurs using gas chromatography with an electron capture detector, high performance liquid chromatography, and other analytical instrumentation. The methods to detect explosives are mostly performed in a laboratory setting, after the investigators have left the scene of interest. If the explosive is detected on-site, the crime scene technicians will have more insight into what they are looking for and what pieces of evidence to collect pre-blast.

The collection of airborne particles and vapors is carried out using a mechanical device such as a pump to draw the vapors into the sampling device, such as a sorbent tube, filter, impinger, or sample bag (7). This filter can consist of various materials depending on the analyte, with common materials being fiberglass, quartz and polyvinyl chloride (PVC). Usually, air cassettes are employed to collect aerosols in question onto filters for analysis at the laboratory. In order to speed up this process and generate results on-site, it is possible to create a filter that has a colorimetric reaction spot to confirm the presence of the explosive of interest before leaving the scene. This colorimetric reaction can be enhanced by the properties of gold nanoparticles.

Nanotechnology is a relatively new field of science and was presented in 1959 by Richard P. Feynman during his lecture “There’s Plenty of Room at the Bottom” (8). Nanoparticles (NPs) are defined by the International Organization of Standardization (ISO) as particles spanning 1-100nm in diameter, smaller than everyday objects but larger than atoms (9). To understand how small these particles are, they can be compared to the thickness of a human head hair; the diameter of a hair is approximately 60μm, or 60,000nm. Nanoparticles are present all around us, such as in printer ink or paint, and there is special interest in its applications in medicine, such as targeted drug delivery. The same characteristics that allow nanoparticles to enable targeted drug delivery can be employed in other fields, such as forensic science. From the development of latent fingerprints to the detection of explosives, nano-devices and nano-sensors are the focus of the nano-forensics discipline (10).

The optical properties that NPs exhibit are one of the main characteristics that attract scientists to their use in an array of applications. Gold nanoparticles (AuNPs) are one of the most versatile NPs studied. The Au nanoparticles exhibit a red color and have a maximum absorbance at 520nm. They often react with the analyte to promote not only a change of color, but also conductivity or surface charge (11). Since these properties are measurable, it is possible to determine a correlation between a change in the properties of the AuNPs and the presence and concentration of an analyte. In addition, nanoparticles do not require extensive materials and instrumentation to be synthesized. The particles can be altered to have the desired shape, size and properties making them adaptable with applications in biology, engineering and chemistry. Gold nanoparticle's biocompatibility and low toxicity make them a preferred material in the area of nano science. The application of the synthesized nanoparticle dictates the type of method needed to create it. Apart from the nanoparticle itself, a functionalized component that reacts with the analyte of interest must be attached to observe a measurable change in the properties of the NPs and use it as a sensor.

Nanomaterials in forensic science are mainly used to develop latent fingerprints and increase the limit of detection for trace materials (12). However, the application of similarly functionalized NPs for explosive detection has been recently studied. Explosive activities have been on the rise across the world, which has led to an increased need to detect trace explosives. (13) Dogs are commonly used to recognize explosive odors, but their acquirement and training is expensive. Other methods of detection and identification of explosives involve the use of analytical instrumentation on samples collected from the scene of interest after it is processed.

Because of this, an alternative is needed to detect explosives on-site. Nanomaterials are the perfect tool to use as sensors for explosive materials, whether detonated or not. (14).

Nanoparticles can be functionalized to react with desired compounds. This happens via the formation of adducts that can change the properties of the nanoparticle employed. For example, the electrochemical and optical properties of NPs can be affected when in the presence of the compound of interest. For TNT, the formation of an adduct when in contact with an amine group has been studied. Electron-rich amine ligands and electron-deficient aromatic ring interactions result in an amine–TNT charge-transfer σ-adduct known as a Meisenheimer complex (**Figure 3**). Further literature study suggests that this σ-adduct forms at the methyl group of the TNT molecule; as a result, a negative charge resonates and is stabilized by three electron withdrawing nitro groups (-NO_2) on the molecule (15). With this being said, it is possible to functionalize a metallic nanoparticle with an amine compound to make it selective for TNT. Two of the compounds that have been functionalized to silica and gold nanoparticles to form this TNT-detecting adduct are cysteamine hydrochloride and ethylenediamine.

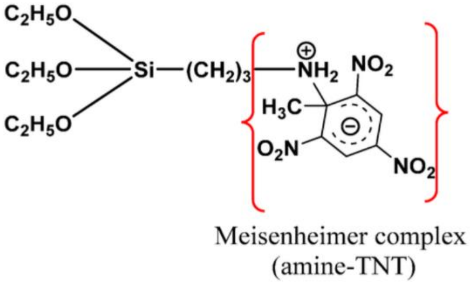

Figure 3. Meisenheimer complex between amine and TNT (15).

The formation of the amine-TNT complex results in a color change from clear to red that confirms the presence of the explosive and will allow for colorimetric analysis. Colorimetry is the detection of compounds through a change in color due to reaction with a chemical reagent. The color change can be measured by eye in the visible range, although spectroscopic detection is often employed for quantitative analysis (16). There are several colorimetry-based explosives detection devices available that require the sample to be in solution. However, the investigators do not always know the location of an explosive when they approach a scene. When this is the case, air sampling of TNT up to nanograms can be employed on-site using portable analytical instrumentation, such as the Ion Mobility Spectrometer (IMS), but this option is rarely used. A colorimetric air filtering technique may provide an alternative solution to this problem, by detecting explosives regularly at airports, concerts, military activities and other points of interest at a lower cost and lower analyte concentrations.

CHAPTER 2: PROJECT GOALS AND OBJECTIVES

In this research project, attempts were made to develop a colorimetric technique based on nanoparticles for the detection of TNT and other nitroaromatic-based explosives using air sampling and testing.

Objective 1

To synthesize amine functionalized gold nanoparticles for the colorimetric detection of TNT with ethylenediamine and cysteamine. The Meisenheimer complex between the TNT and the amine functionalized gold nanoparticles should allow for picogram detection of trinitrotoluene in solution.

Objective 2

To functionalize different filter membranes (fiberglass, quartz, cellulose fiber) by coating with cysteamine, EDA and the developed nanoparticles to detect the presence of TNT explosive in the air at low concentrations. A color change to red in the presence of TNT should occur on both cysteamine and ethylenediamine coated filters. Meanwhile, a color change from red to blue should be evident when the TNT is exposed to filters functionalized with Au-amine nanoparticles.

Objective 3

Demonstrate the proof of concept and optimize the nanosensor for improved sensitivity and selectivity. This involves the development of limit of detection of both TNT and amine concentrations by visual recognition of the expected color change.

CHAPTER 3: METHODS AND MATERIALS

Reagents and Materials

Hydrogen tetrachloroaurate ($HAuCl_4 \cdot 3H_2O$), trisodium citrate, cysteamine hydrochloride, ethylenediamine, 2,4,6-Trinitrotoluene in acetonitrile standard, sodium borohydride and acetone were purchased from Sigma Aldrich (USA). All chemicals and solvents were of analytical grade and were used without further purification. Filter papers of different composition, including glass fiber, quartz, polytetrafluorethylene (PTFE) and cellulose fiber (Whatman), were purchased from SKC INC. A 2,4,6-Trinitrotoluene (TNT) stock solution (5mM in acetone) was a gift from Chad Schennum at the Virginia Department of Forensic Science. Distilled water was used for dilutions throughout the experiments.

Instrumentation

The transmission electron microscopy (TEM) images were obtained from a JEM-1400 Plus TEM from the VCU Microscopy Core. UV-vis absorption spectra were collected using a BioTek Cytation 3 Plate Reader with Gen 5 software. Particle size and zeta potential measurements of the particles were collected using a Malvern ZetaSizer ZS90. Mass measurements were taken with either a Sartorius TE153S balance or an A&D BM-22 ultramicrobalance. A SKC Aircheck Touch 220-5000TC air sampling pump was used for particle collection onto the filters.

Au NPs Synthesis

The gold nanoparticles were synthesized using the classical Turkevich synthesis method. The general synthesis methodology is as follows, a 50mL solution of 10mM and a 100mL 1%

trisodium citrate stock solution was prepared in MilliQ water. Ten milliliters of the 10mM gold chloride solution were left to boil (~100°C) without reflux while stirring at 700rpm in a 20mL glass scintillation vial. At its boiling point (~100°C), 1mL of the 1% trisodium citrate solution at room temperature (22±1°C) was added to initiate nanoparticle nucleation and growth. Particle formation was indicated by the solution turning from yellow (gold chloride) to purple (gold seeds) to a deep burgundy red (gold nanoparticles). After 15 minutes, the solution was removed from heat and cooled to room temperature (22±1°C). Gold nanoparticle formation was confirmed by UV-VIS spectroscopy measuring a maximum absorbance at 520nm. The particle size (hydrodynamic diameter) and zeta potential (surface charge) were measured using TEM, dynamic light scattering (DLS) and electrophoretic mobility. Measurements were performed in triplicate to ensure reproducibility and uniformity of nanoparticle characteristics.

Au NPs Surface Functionalization

Cysteamine Modification

The amino functionalized gold nanoparticles were prepared by a slight modification of the widely used synthesis procedure reported (21). This included the addition of 400μL of 200mM cysteamine hydrochloride solution to 40mL of 1.5mM $HAuCl_4$ solution. This mixture was left to stir at 800rpm for 20 minutes at room temperature (22±1°C). A 500mL10mM sodium borohydride solution was freshly prepared with distilled water and 10μL was added to the gold chloride solution. The reagents were left stirring for 20 minutes at 700rpm in the dark and at room temperature (22±1°C). The presence of the wine-red solution indicated nanoparticle formation. To confirm functionalization of the amine to the surface of the nanoparticle, their zeta potential was measured using the Malvern ZetaSizer.

Ligand Exchange

Equal volume (500µL) of 6.54×10^{-11} particles/mL of gold nanoparticles and cysteamine (1×10^{-6} M) were added to a microcentrifuge tube for functionalization. This mixture was vortexed for a minute and left at room temperature (22±1°C) for 24 hours.

Ethylenediamine Modification

A different published approach to functionalize gold nanoparticles with amine was also explored. (22) This one consisted of taking 700µL of the citrate capped nanoparticles and adding 100µL of 1×10^{-6} M EDA to this one. The mixture was left stirring for 12 hours. Similar to the cysteamine modification, the size and charge of the nanoparticles was measured.

TNT Dilutions

Several dilutions of the 5mM TNT in acetone stock solution were made with acetone. These dilutions of TNT in acetone had concentrations of 3mM, 1mM, 500µM, 300µM, 100µM and were chosen due to the intensity of the expected color change after consulting with the literature. (3)

Filter Preparation

Several filter paper compositions including fiberglass (SKC Type AE 1.0µm), quartz (SKC Type R-100 1.2µm), polytetrafluoroethylene (PTFE) and cellulose fiber (Whatman qualitative filter paper) were tested for the adsorption of gold nanoparticles. The filters were stored at 22±1°C and 36% relative humidity (RH) in an environmental chamber for at least 24 hours then weighed using an ultramicrobalance before adding 1mL of Au-amine NPs to its surface. They were left on a Kimwipe covered with a petri dish at room temperature (22±1°C) to dry for 24hrs. After drying the filters were stored at 22±1°C and 36% RH in an environmental chamber for at least 24 hours then weighed again to determine the adsorbed mass. This process was also carried out for filters with the reagents used, which were prepared by adding 1mL of citrate-coated Au NPs, 1mL of $1x10^{-6}$mM EDA or 1mL of $1x10^{-6}$mM Cysteamine.

Dynamic Light Scattering Sample Preparation

A 1mL plastic cuvette containing 100µL of sample and 900µL of deionized water was used for measurement of hydrodynamic diameter of the gold nanoparticles. This analysis was performed at room temperature (22±1°C). To determine the zeta potential of the nanoparticles, a MALVERN 1mL folded capillary cell was used in a similar matter. Triplicate measurements were collected for each sample.

UV-Vis Spectroscopy Sample Preparation

A volume of 200µL of each sample was added into different wells of a Fisherbrand 96 well plate. Ultra-Violet to Visible spectra measurements were taken of only 10µL of sample using a micro-volume plate. Measurements were taken every 10nm across a wavelength range of 230-700nm. Maximum absorbance values of gold nanoparticles were measured at 520nm.

Transmission Electron Microscopy Grid Preparation

To study the morphology of the gold nanoparticles, 10µL of the sample was added to a PELCO carbon coated copper grid and left to dry on a Kimwipe covered by a Petri dish for at least 24 hours before being taken to the VCU Microscopy Core for imaging.

Air Sampling

Using a SKC Air pump, air was sampled using four types of prepared filters (amine functionalized AuNPs, AuNPs, EDA, Cys). Air was pulled through each filter for 5 hours at a rate of 2.5L/min. Air was also pulled through a glass impinger filled with 5mL of 5M EDA solution at a rate of 2.5L/min using a SKC air pump to sample TNT vapor.

Nebulization of TNT

The nebulization of 5mL of TNT (3mM) using an atomizer onto different EDA filters (5M) was studied at different distances (1, 2, 3, 4 feet) in the fume hood. A total of 3 pumps of spray were used for each distance test.

CHAPTER 4: RESULTS & DISCUSSION

Nanoparticles

Gold Nanoparticles

The synthesized citrate capped gold nanoparticles were used as a control for the subsequent studies. The resulting solutions exhibited a wine-red color. The UV-Vis spectra confirmed the nanoparticle formation and exhibited a maximum average optical density of 2.18 at the absorbance peak wavelength of 520nm, shown in **Figure A2**. In addition, the gold nanoparticles exhibited a Z-average hydrodynamic diameter of 31.5d.nm ±1.4d.nm with a polydispersity index (PDI) of 0.5± 0.1. **Figure A3** portrays the size distribution by intensity of the gold nanoparticles synthesized using the Turkevich method. The zeta potential of the gold nanoparticles was -28.2 ± 0.6 mV. This negative charge is due to the citrate coating of the gold nanoparticles. The morphology of these nanoparticles was studied using TEM with images taken at 120kV (scale bar = 50nm). The nanoparticles are uniform and spherical in shape, and their diameter is consistent with the DLS size measurements previously taken.

Amine Functionalized Gold Nanoparticles

Cysteamine

The synthesized nanoparticles with cysteamine exhibited a size of 56.2d.nm ± 0.89d.nm and an average PDI of 0.24 ± 0.01 (**Figure A5**). The zeta potential of these nanoparticles was +25.6mV ± 0.5mV. This positive zeta potential indicates that the functionalization of amine to the surface of the gold nanoparticles was successful. The average maximum absorbance peak of these nanoparticles was at a wavelength of 520nm and optical density of 1.15 ± 0.022 (**Figure A4**). Knowing that cysteamine contains a thiol group, which has a higher affinity to gold than the carboxyl groups in citrate, a ligand exchange should occur producing cysteamine functionalized AuNPs. After adding equal amounts of cysteamine hydrochloride at different concentration to citrate capped gold nanoparticles, several things were noted. Firstly, at higher concentrations of cysteamine hydrochloride, the gold nanoparticles aggregate and turn form wine-red to blue. The lowest concentration when this aggregation does not occur is at 0.02mM. In addition, the presence of cysteamine to the surface of the nanoparticles should exhibit a positively charged nanoparticle. However, when determining the zeta potential of these nanoparticles they were negative (-18.9±0.5mV). This indicates that the ligand exchange and functionalization of amine to the surface did not occur.

When adding 5mM TNT to the cysteamine functionalized gold nanoparticles to test for the color change due to the formation of the Meisenheimer complex between the electron deficient nitroaromatic ring of TNT with an electron rich amine, no visible color change occurred. The literature review mentioned that this solution needs to be at a pH of 8.5 to prevent the cysteamine from forming its cyclic form (**Figure 4**), which happens at pH=7 and prevents a reaction with the TNT. The pH was modified with 10M sodium hydroxide to reach 8.5 and the

TNT was added. However, because the expected results and color change still did not occur, ethylenediamine was chosen as an alternative for functionalization of the nanoparticles.

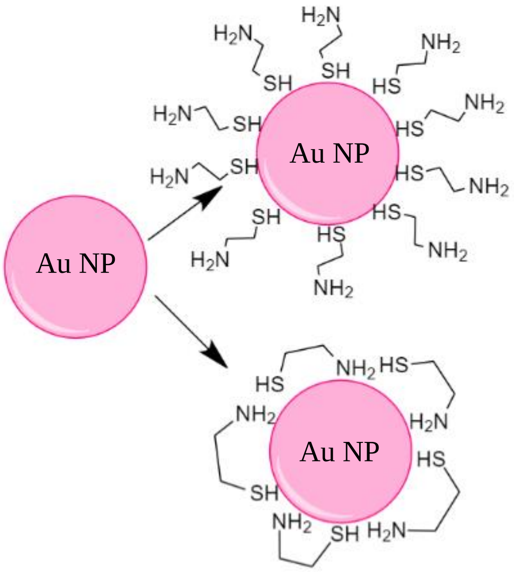

Figure 4. Cysteamine functionalized gold nanoparticles configurations.

Ethylenediamine

Other published articles have mentioned the use of ethylenediamine as a capping agent for gold nanoparticles. Ethylenediamine contains two amine groups and is reported to also produce a color change due to formation of the Meisenheimer complex with TNT. The colorimetric reaction of EDA and TNT was explored at various concentrations. The lowest TNT concentration at which this color change was visible to the naked eye was 1M. Similar to cysteamine, when high concentrations of ethylenediamine are added to gold nanoparticles, they aggregate and exhibit a blue color. The smallest concentration of EDA where this does not occur is at $1x10^{-6}$M, which is the concentration that was used for ligand exchange of citrate to ethylenediamine to functionalize the gold nanoparticles. Because gold has a higher affinity for amine groups than carboxyl groups, ethylenediamine should successfully exchange with citrate.

A complication involves the possibility of both amine groups coordinating with the gold surface versus one, as depicted in **Figure 5**. This is reported to occur at concentrations above 1×10^{-6} M where the diacid form of ethylenediamine is abundant, resulting in aggregation of the nanoparticles. At lower concentrations, the monobasic acid configuration of EDA allows for the attachment of the protonated amino group to the surface of the gold nanoparticle (22). After successfully functionalizing amine to the surface of the gold nanoparticles, TNT should promote aggregation of the nanoparticles when added due to the strong donor-acceptor interactions between amine and TNT. However, this aggregation was not visible in the tests carried out and was not observed after performing TEM imaging.

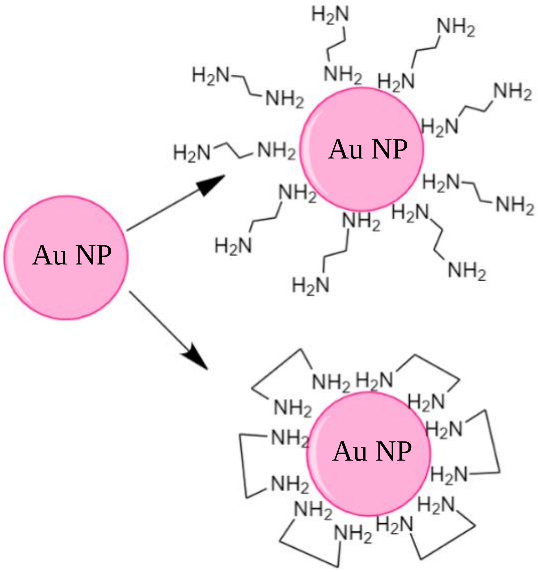

Figure 5. Ethylenediamine functionalized gold nanoparticles configurations.

Filters

To study whether the gold nanoparticles could be synthesized onto filters, the nanoparticle synthesis was conducted in a beaker containing a quartz filter. After completion of the synthesis reaction, the resulting gold nanoparticles appeared to have covered the surface of the filter. No evidence suggested that this method had an advantage over drop casting the nanoparticles onto the filter after synthesis. For this reason, subsequent trials were performed by drop casting the gold nanoparticle suspension directly onto the filters.

Fiberglass, quartz and cellulose fiber membranes were coated with ethylenediamine at different concentrations and left to dry over 24hours to study if TNT vapors would promote a color change without using gold nanoparticles to enhance the visible color signal. When TNT in acetone is dropped to these filters a visible red-orange color appears, indicating the presence of the Meisenheimer complex. These filters were also placed in a cassette and TNT air sampling at 2.5L/min for 5 hours was carried out. No visible color change occurred when this method was employed. Furthermore, TNT in acetone vapor was also sampled into an EDA solution using an impinger. No color change was observed after 1 hour, indicating that there was not enough TNT present in the vapor to produce the expected color change of the reaction.

On the other hand, 2mL of 3mM trinitrotoluene were aerosolized and sprayed at different distances onto a cellulose fiber (Whatman) membrane containing EDA and a color change did occur instantaneously after the TNT droplets came in contact with the filter. After the acetone solvent evaporated, this color change persisted. This study provides information on how TNT travels at different distances when sprayed onto a surface.

CONCLUSIONS

In this project, amine functionalized nanoparticles were made using ethylenediamine and cysteamine. Aggregation of the gold nanoparticles was expected to occur in the presence of TNT and yield a blue-purple color. Due to the nature of the TNT, and reagents, including pH, solvents and manufacturing dates, this reaction was not visible to the naked eye. However, the TNT acetone solution did yield a visible red color when in contact with ethylenediamine. Interestingly, opposite of reported literature, the cysteamine did not have this effect on TNT and could be attributed to the cysteamine structural confirmation at different pH values. In addition, the air sampling of TNT at different concentrations did not result in a color change of any of the filters studied. This may be attributed to the low vapor pressure of TNT. Vapors of TNT solution were also sampled using an impinger to deposit the particles in EDA solution but again, no visible reaction occurred. On the other hand, the nebulization of TNT onto different EDA (5M) filters was studied and a color change did occur. This color change was visible at the lowest concentration used of TNT (1mM) and at a sampling distance of approximately 3 feet. The resulting color change indicated that TNT traveled with the solvent and as the solvent evaporated; the color change reaction persisted. These observations allowed for information on how TNT can be detected and new methodologies for sensing 2,4,6-Trinitrotoluene on-site can be studied and optimized for further application.

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APPENDIX A: ADDITIONAL TABLES AND FIGURES

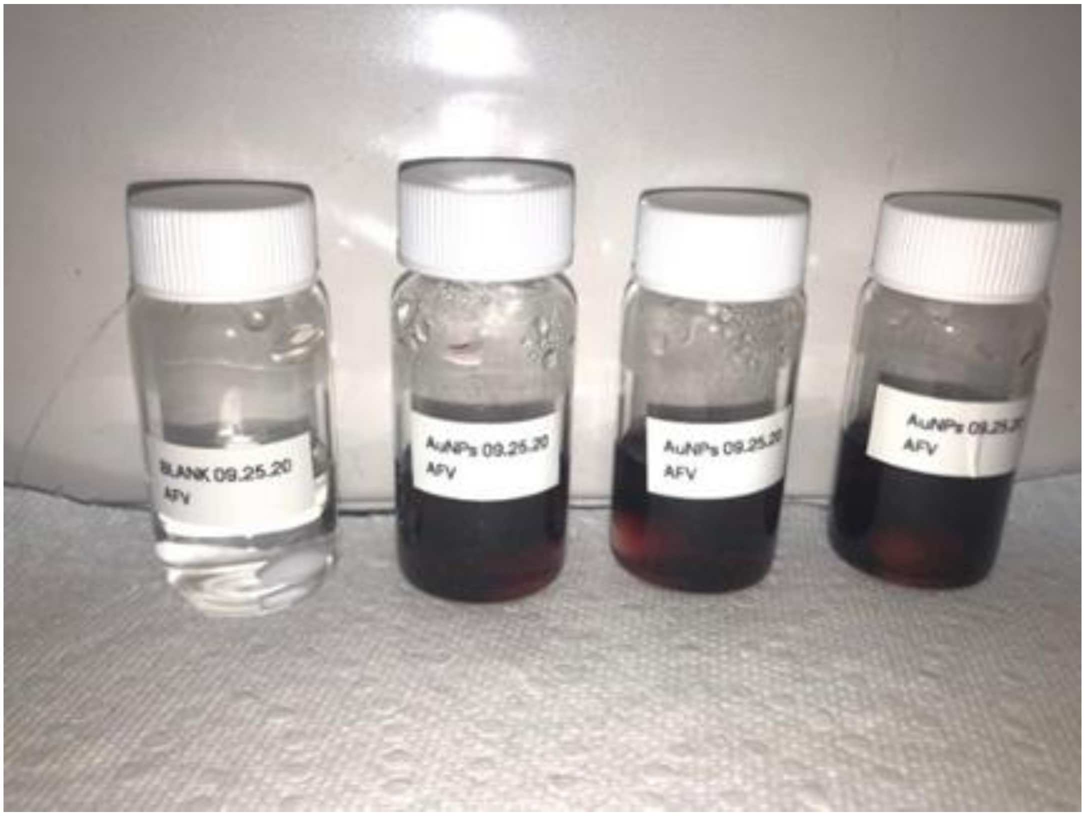

Figure A1. Gold nanoparticles synthesized by the Turkevich method.

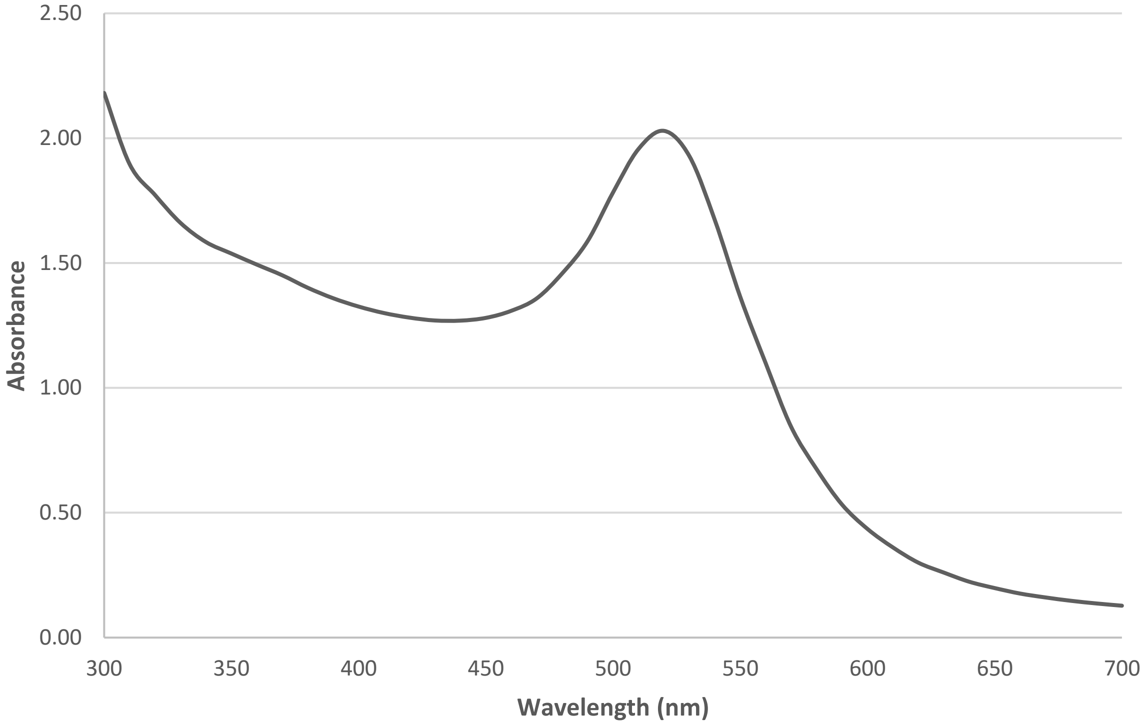

Figure A2. Absorbance spectra of Au NPs
synthesized by the Turkevich method.

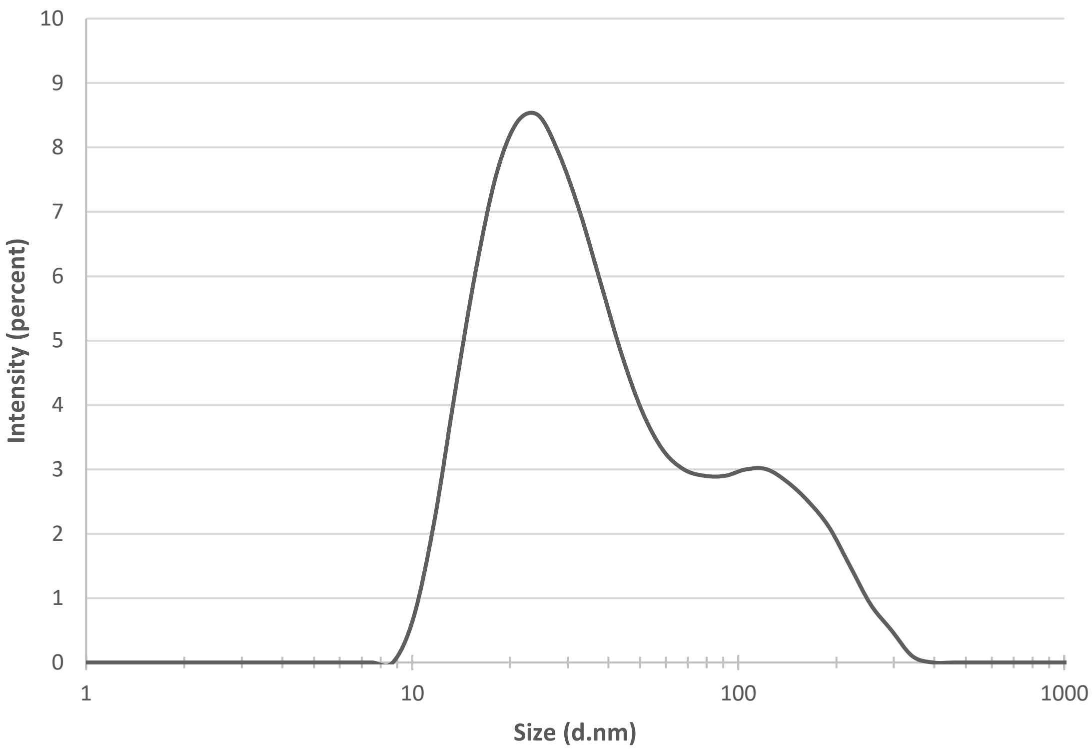

Figure A3. Size measurement of Au NPs synthesized by the Turkevich method.

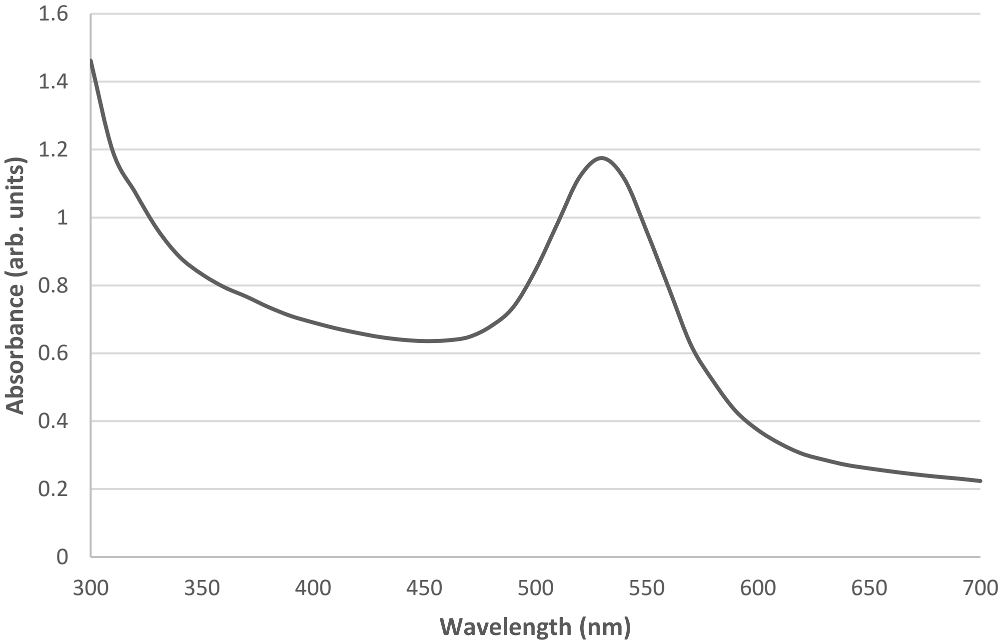

Figure A4. Absorbance spectra of Au-Cys NPs.

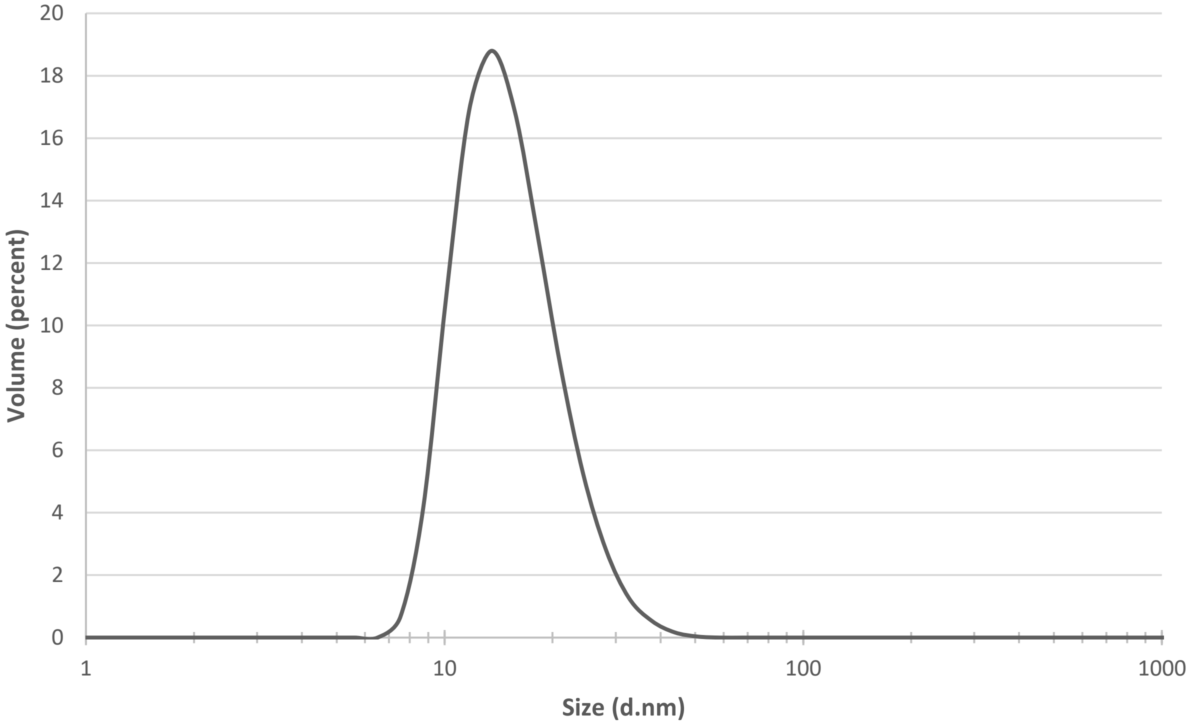

Figure A5. Size measurement of Au-Cys NPs.

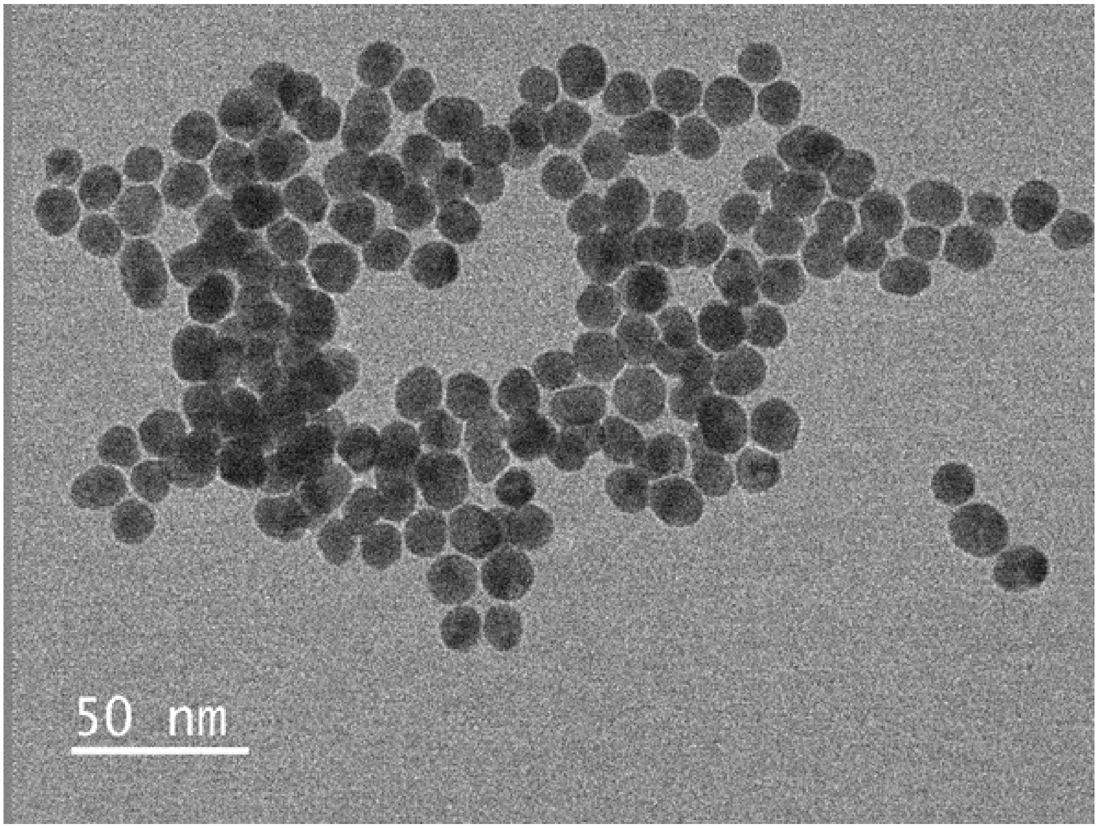

Figure A6. TEM image of Au NPs
synthesized by the Turkevich method.

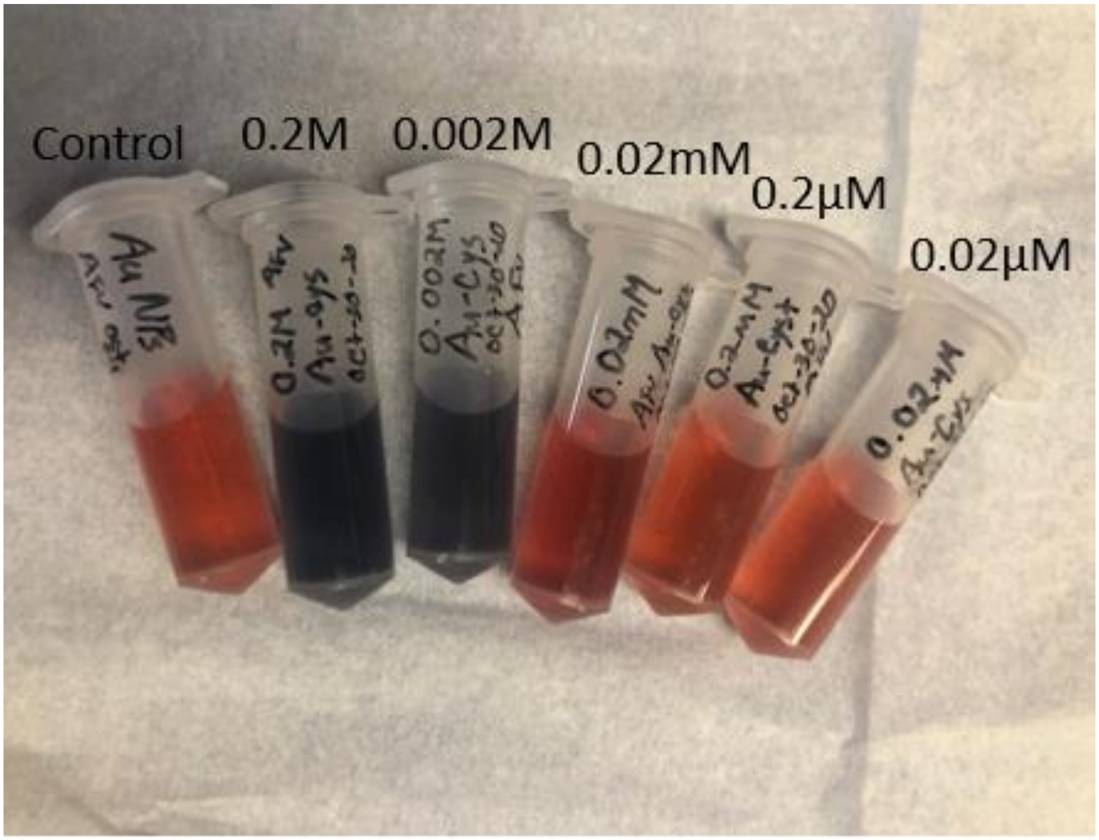

Figure A7. Au-Cys NPs synthesized via ligand exchange at different concentrations.

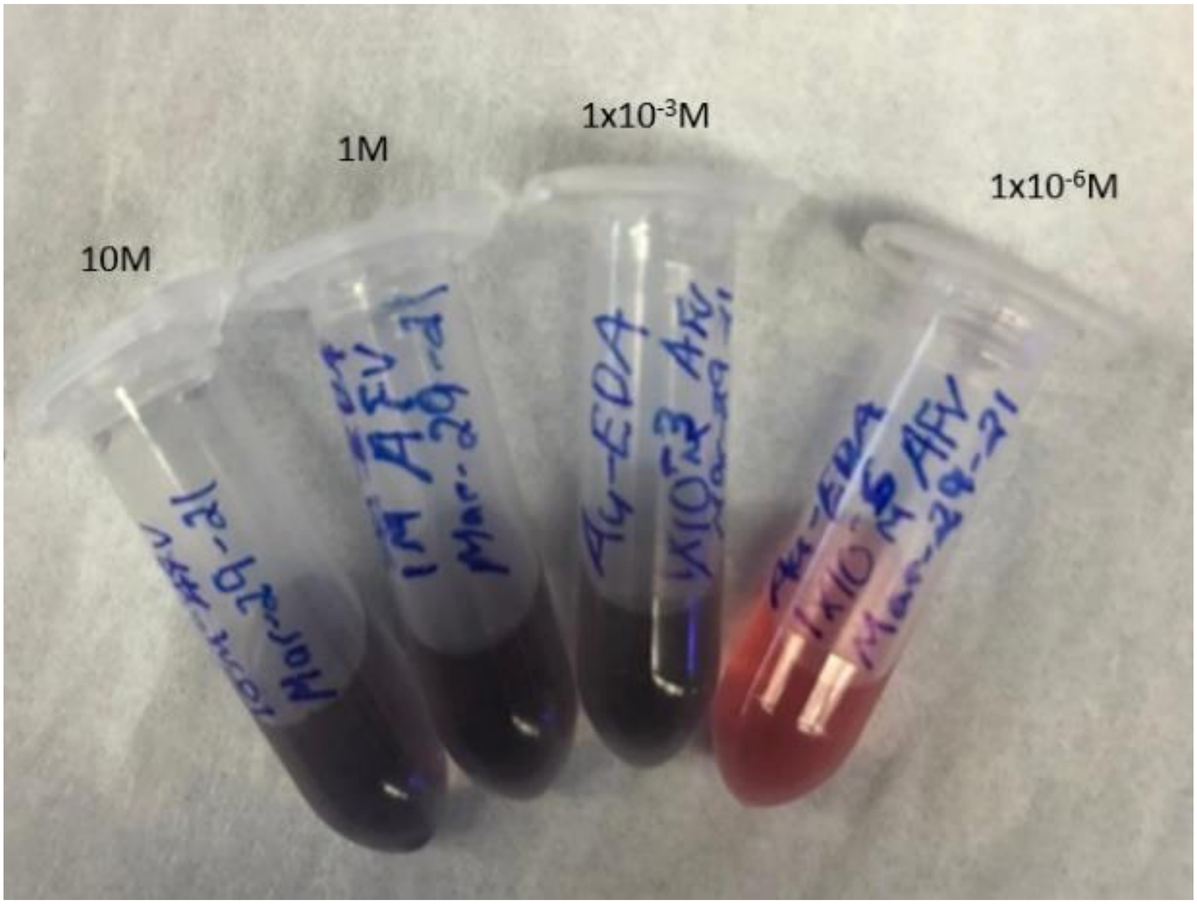

Figure A8. Au-EDA NPs synthesized via ligand exchange at different concentrations.

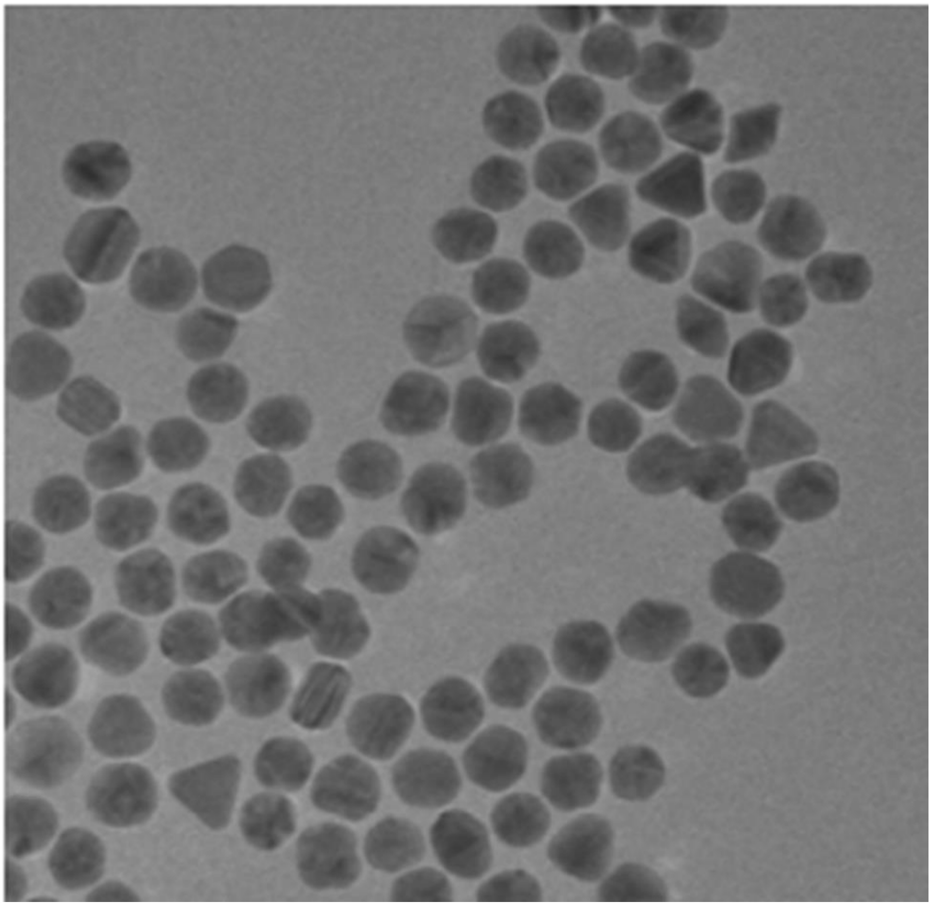

Figure A9. TEM image of Au-EDA-TNT
(Scale bar 50nm).

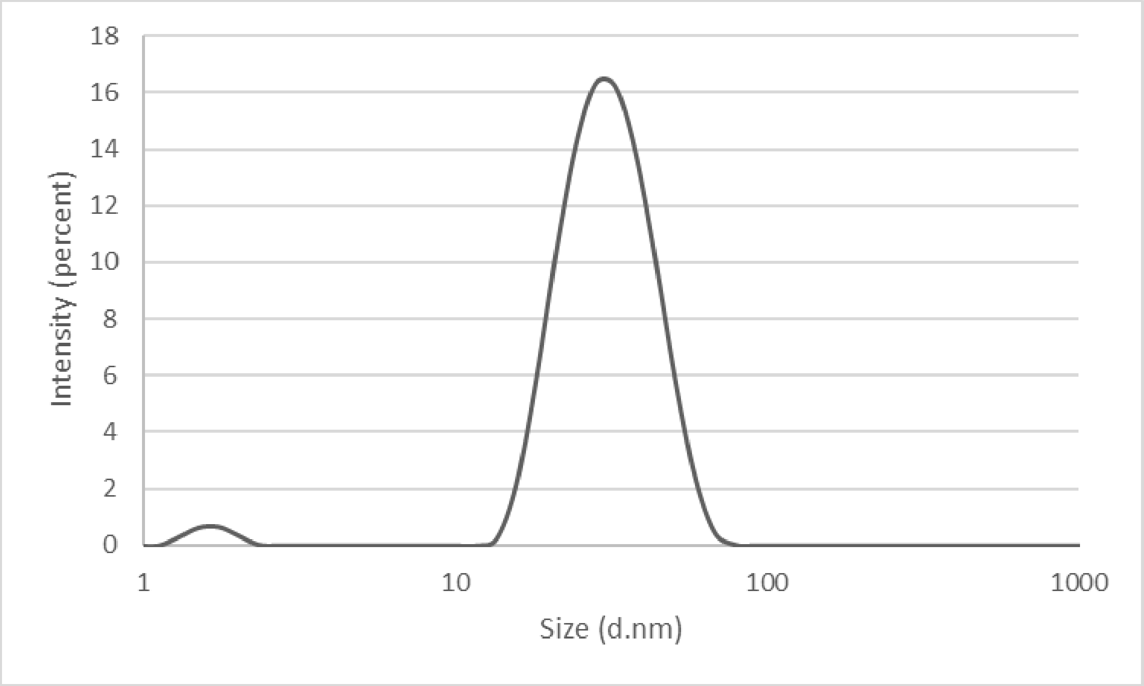

Figure A10. Size measurement of Au-EDA NPs.

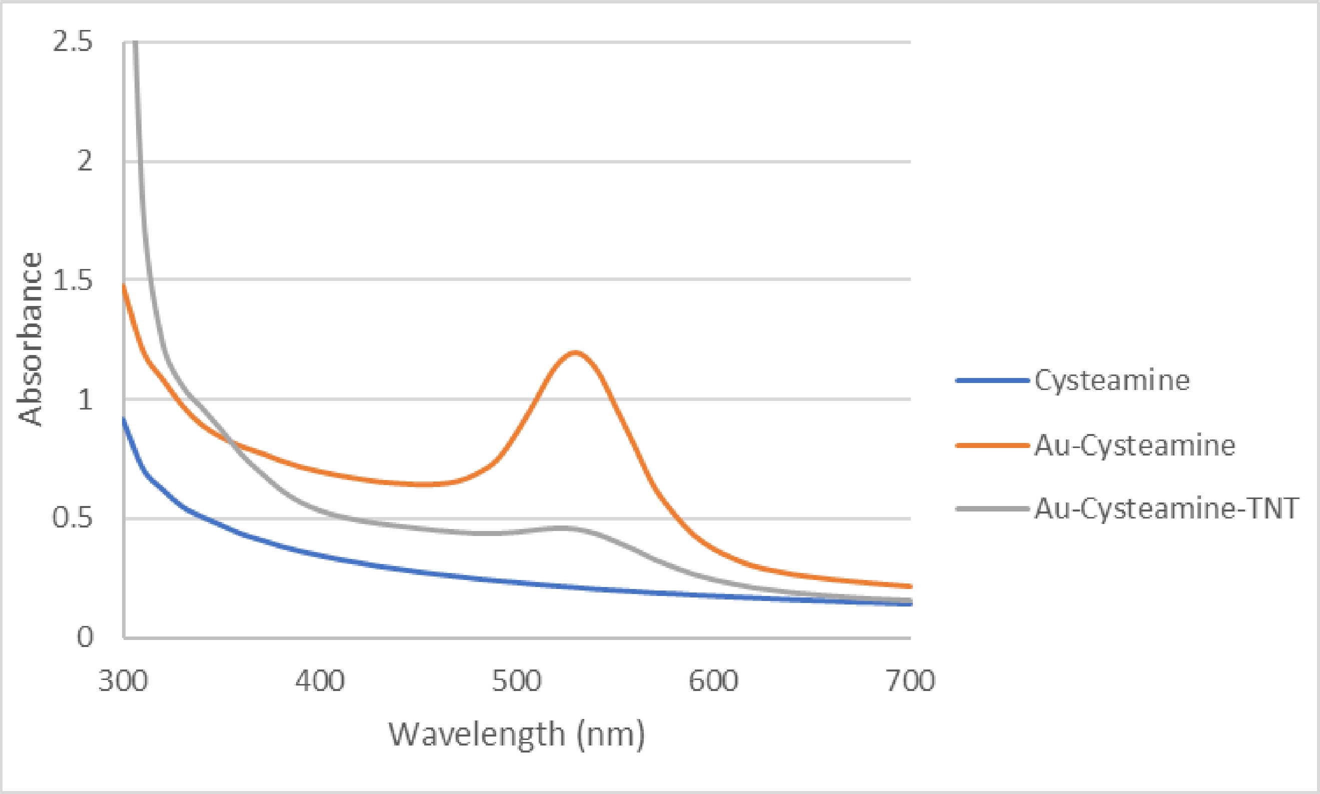

Figure A11. Absorbance measurement of Cysteamine, Au-Cys and Au-Cys-TNT.

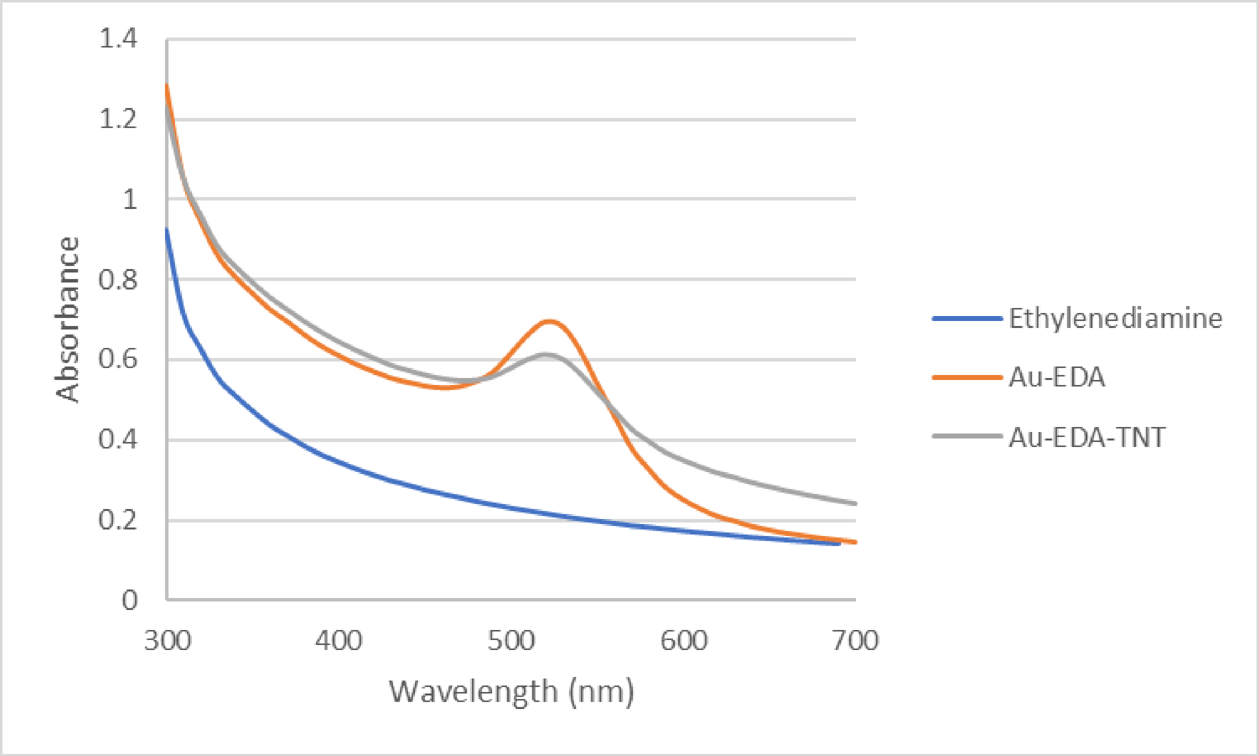

Figure A12. Absorbance measurement of
Ethylenediamine, Au-EDA and Au-EDA-TNT.

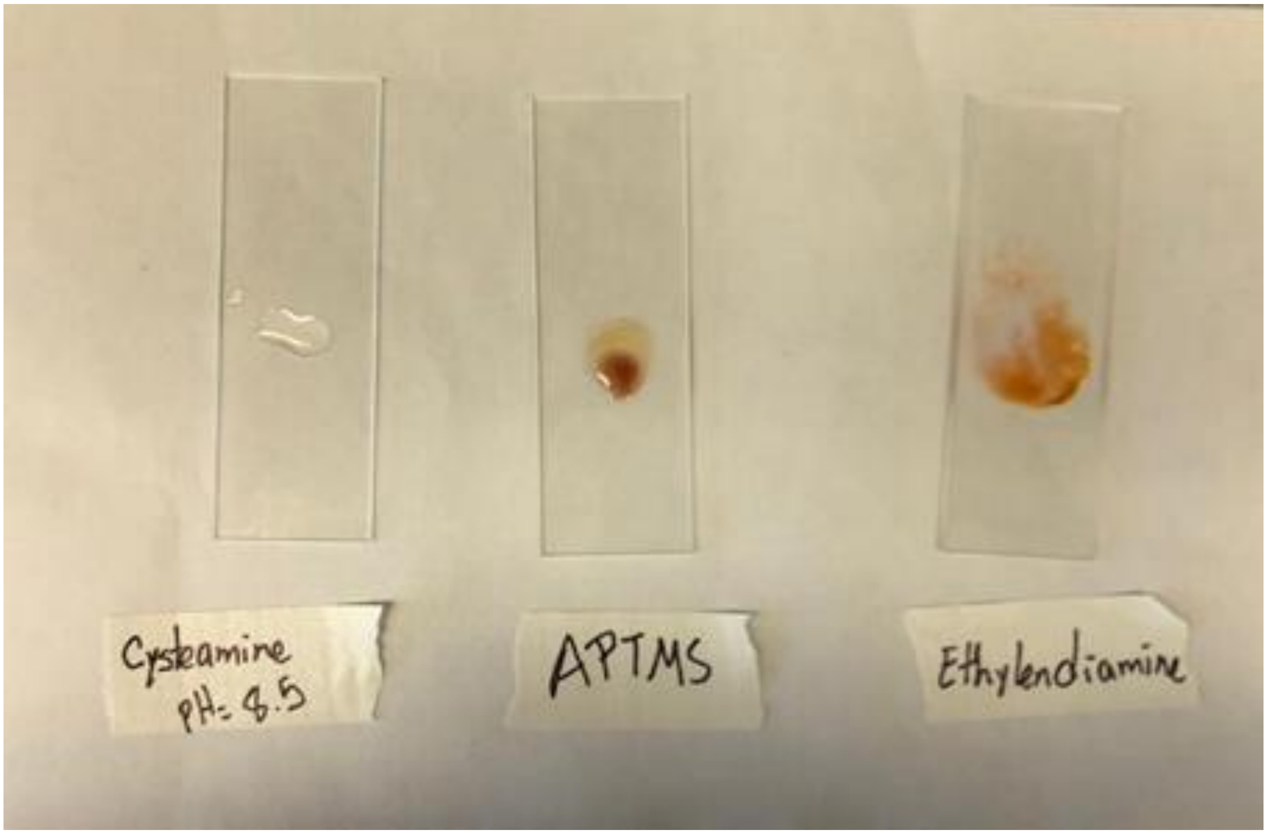

Figure A13. TNT colorimetric reaction with Cysteamine, APTMS, Ethylenediamine.

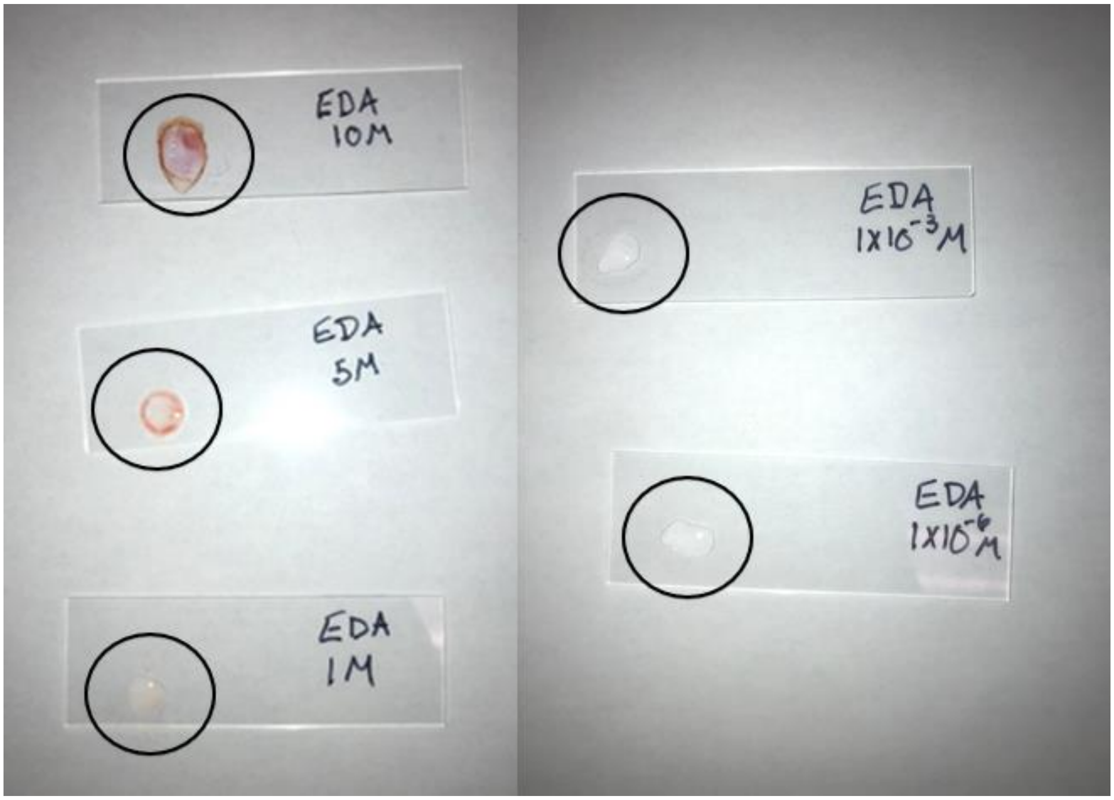

Figure A14. TNT colorimetric reaction with Ethylenediamine at different concentrations.

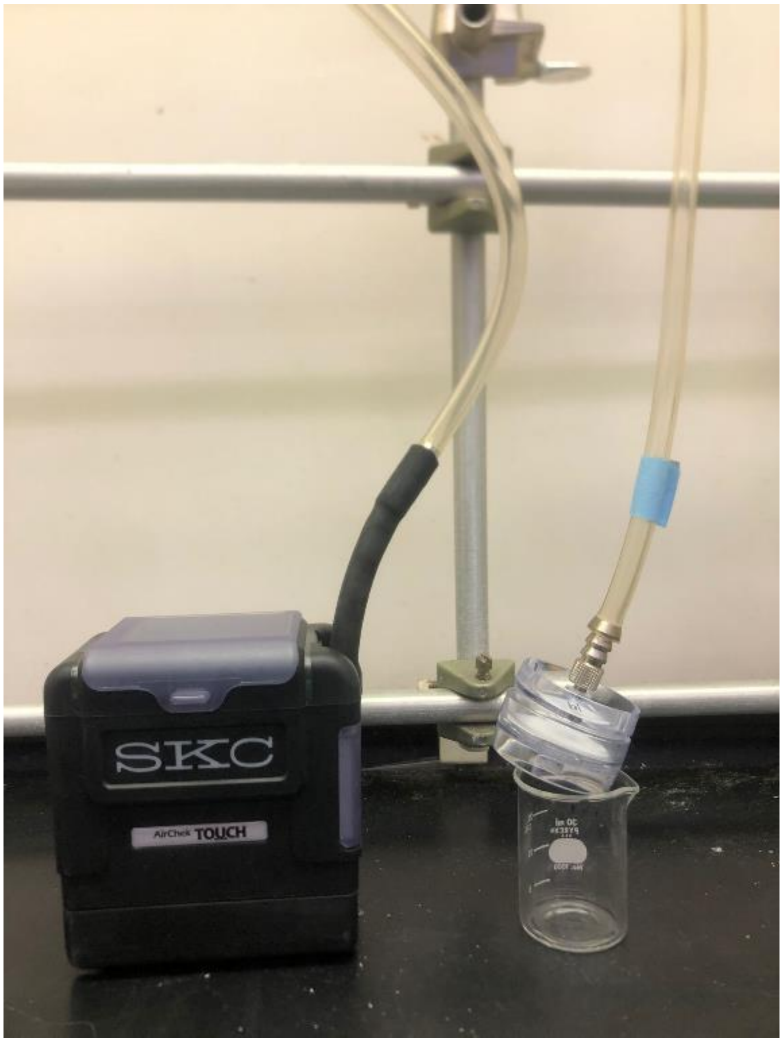

Figure A15. Air filtering method set-up.

Figure A16. Impinger method set-up.

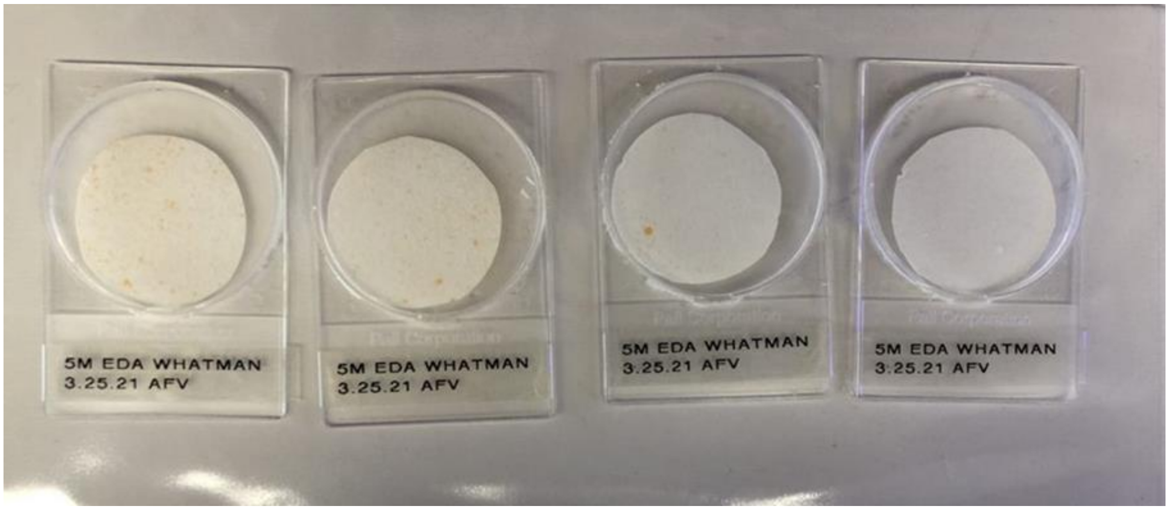

Figure A17. 5M EDA filters with sprayed TNT at different distances.

APPENDIX B: VITA

Andrea Isabel Ferrer Vega was born on October 8th, 1997 in San Juan, Puerto Rico, and is an American citizen. She graduated from C.R.O.E.M High School in Mayagüez, Puerto Rico in 2014. That summer she participated in her first experience as a paid researcher at The University of Texas at El Paso. After this, she continued her studies at the University of Puerto Rico where she received her Bachelor of Science in Chemistry in 2019. In addition, she is a certified and licensed high school science teacher in Puerto Rico. Subsequently, she was accepted into the Forensic Science Master's program at Virginia Commonwealth University in 2019 where her area of specialization is in Forensic Chemistry and Trace Analysis. In efforts to be a well-rounded student, she accepted a research assistant position in the College of Engineering at VCU under the tutelage of Dr. Nastassja Lewinski where she worked on nanoparticle synthesis for targeted drug delivery. Along her academic career she has also been a research mentor in the areas of biomathematics, genomics and applied math. In addition, she has participated in many research projects and has presented at symposiums and conferences including the ACS Annual Green Chemistry & Engineering Conference and the Third Annual Virginia NanoMedicine Symposium on Engineered Health. After her Master's degree she plans on working at the Institute of Forensic Science in Puerto Rico as a forensics examiner.