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**Determination of Cadmium and Gold Concentrations  
Utilizing Neutron Activation Analysis**

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4 April 2005

## Executive Summary

The purpose of this experiment was to build a baseline for comparison for cadmium and gold concentrations using neutron activation analysis. This baseline can be used in the future to find the concentration of cadmium and gold in samples with unknown concentrations such as determining the amount of these elements in aerogels that are being used to absorb these metals out of solution.

Neutron Activation Analysis was used by bombarding samples of known concentrations of cadmium and gold with neutrons using the UMR reactor. Then the radiation emitted from the activated isotopes could be measured using a germanium detector and a trend established for various concentrations of these elements.

The samples were solutions of cadmium and gold ranging from  $5E-5$  molar to 1.0 molar solutions. These samples were packaged using centering devices in the vials to ensure that the samples were irradiated in the same manner time after time. The samples were then irradiated at 20 kW or in a thermal flux of approximately  $1.86E11$  n/cm<sup>2</sup>/s. The irradiation time varied depending on the metal – 15 seconds for cadmium and 30 seconds for gold.

The samples were then counted on a germanium detector again using centering devices to ensure consistent placement of the samples relative to the detector. The samples were counted for 10 minutes of live time. Live time counts compensate for the time the detector is busy from detecting a previous count.

The gold samples consisted of two different chemical formulas. The first was H<sub>2</sub>AuCl<sub>4</sub> and the second was KAuCl<sub>4</sub>. These two different sets created different results, which was not expected because NAA is independent of the chemistry of the substance. The conclusion was that one of the sample sets was incorrectly prepared but at this point, which set was incorrect has not been determined, but both samples followed the same linear trend.

Cadmium and gold were both easily detectable using NAA. The trend for both of these materials was linear which agrees with the theory for short irradiations such as these. The standard deviation of most of the sample sets was between 2.5% and 5.0%. The only sets that did not fall within this range had too few samples to create an acceptable statistical base.

NAA should be able to be used to detect cadmium and gold in unknown samples without difficulty. The baseline created here can be used in the future to determine the concentration of these elements in unknown samples.

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## Introduction

The purpose of this project is to show that neutron activation analysis (NAA) can be used to quantitatively determine the amount of various metals in a sample. This project specifically addresses Cadmium and Gold and their detection using NAA.

This project has the goal of building a baseline comparison from samples containing Cadmium and Gold in known concentrations. The results from this project may be used to determine the amount of Gold and Cadmium collected in aerogels that are being used to trap metals such as cadmium and gold out of solution.

## Background

Neutron activation analysis (NAA) is a qualitative and quantitative method of identifying elements that make up a sample. The elements present can be identified by the types of radiation they emit, the energy of the radiation, its intensity, and the half-life. For this research gold and cadmium were irradiated to create a benchmark for their detection<sup>1</sup>.

The first step is to determine the nuclear reaction that will take place and be measured. In this case the University of Missouri Rolla Reactor was used as a neutron source for irradiation so (n,γ) reactions were used. In this reaction the sample is bombarded by neutrons in the reactor and some of the sample atoms absorb neutrons and are activated to an excited state. The two reactions used are shown below in Eq. 1 and Eq. 2<sup>2</sup>.



The sample is packaged and irradiated in the reactor as specified in the procedure. The sample is irradiated and the excited nuclei then release their energy by giving off gamma radiation that can then be measured using a high purity germanium detector attached to a Multi-Channel Analyzer. Each isotope has specific energies that it emits, and the energy and intensity can be recorded by the gamma spectroscopy system.

When a sample is irradiated the activation of the sample is given by the activation equation as shown in Eq.3. This equation assumes that a small number of the target nuclei are transmuted so that the total number of target atoms stays essentially the same. This also assumes that the isotope formed is destroyed by decay only and not by neutron absorption. Finally, this formula also assumes that the flux is uniform throughout the target.

$$A(t_0) = a_i N_i \sigma_i \phi (1 - e^{-\lambda_i t_0}) \quad (\text{Eq. 3})$$

Where:

- $A(t_0)$  = Activity after irradiation
- $a_i$  = Weight fraction of an isotope of interest
- $N_i$  = Number of atoms of the element of interest in the sample
- $\sigma_i$  = Cross section for the reaction of interest
- $\phi$  = Thermal neutron flux
- $\lambda_i$  = Decay constant for element created
- $t_0$  = Irradiation time

## Equipment Used

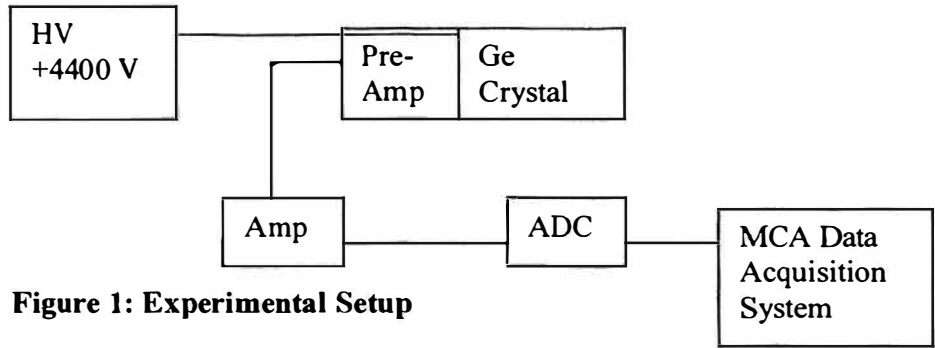
The Equipment used to take the measurements is shown in Table I along with their electronic settings. The equipment shown in the table is the equipment used with the germanium detector at the UMRR.

**Table I: Type, Manufacturer, Model and Settings of Equipment Used**

<b>Instrument</b>	<b>Type</b>	<b>Manufacturer and Model</b>	<b>Electronic Setting</b>	<b>Remarks</b>
<b>Detector</b>	Ge	CANBERRA		
<b>HVPS</b>		CANBERRA Model 3105	+4400 V	
<b>Preamplifier</b>		CANBERRA		
<b>Amplifier</b>	Fast Spectroscopy	CANBERRA 2024		
<b>Analog to Digital Converter (ADC)</b>		Canberra 8077	0.3 V discrimination	
<b>NIM Bin</b>		CANBERRA Model 2000		
<b>Data Acquisition Software</b>		CANBERRA Genie 2000 Version 1.3, May 15, 1999		

The system at the reactor is constantly setup with the high voltage applied and the detector cooled with liquid nitrogen. The signal originates from the Ge crystal where a gamma interaction creates an electron and a hole. The electron and hole then move under the influence of the electric field and are collected. The pulse is then amplified about 10

times and impedance matched to the amplifier by the preamplifier. The amplifier then amplifies the signal about 1000 times. The signal then goes to the Analog to Digital Converter (ADC) that changes the pulse into a channel number and then a count is stored in that channel by the Genie 2000 program. Figure 1 shows a diagram of the experimental setup.



**Figure 1: Experimental Setup**

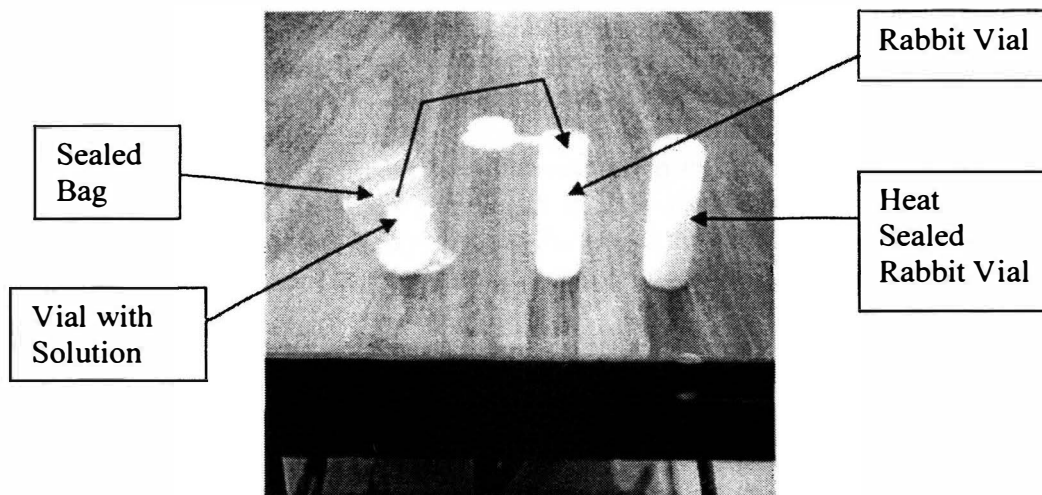
## Procedure

The first step is to have the solutions to be irradiated prepared. Different concentrations of both cadmium and gold were prepared and irradiated. Concentrations tested for both Cadmium and gold are shown in Table II.

**Table II: Concentrations of Gold and Cadmium Irradiated**

	Chemical Form	Concentrations Tested (M)	Irradiation time
<b>Cadmium</b>	CdNO <sub>3</sub>	0.001, 0.01, 0.1, 0.25, 0.5, 1.0	15 seconds
<b>Gold</b>	HAuCl <sub>4</sub> & KAuCl <sub>4</sub>	5E-5, 1E-4, 5E-4, 1E-3, 2E-3, 1E-2	30 seconds

After the solutions are prepared the next step is to package the sample. NAA is very sensitive to contamination so this step is very sensitive requiring very careful handling to ensure that neither the sample nor the packaging gets any foreign substances on them. The packaging was mostly made of thermoelastic polymers, most of which were composed of polyethylene. This makes an excellent packaging material because it absorbs very few neutrons and is very light which makes it capable of being used in the reactor's pneumatic transfer system for irradiation. Problems arose with consistency of the results so a centering device was created for use in the vial used in the pneumatic transfer system and kept the sample centered in the vial at all times. Figure 2 shows the different packaging used, but does not show the centering device.



**Figure 2: Sample Irradiation Configuration**

Each of the small vials with the solution was filled with 1.0 ml of the solution to be irradiated and then sealed in the plastic bag shown. This was then placed in the centering device that is not shown, which was then placed in the rabbit vial and heat-sealed. The centering device for the rabbit vial was deemed necessary after consistent results could not be obtained without it. The centering device keeps the small vial centered in the rabbit vial at a consistent height. This way no matter how the vial is placed next to the reactor, the sample will always be the same distance away from the core. Each of the different pieces of packing are thoroughly cleaned with rubbing alcohol and handled with gloves prior to being packaged to ensure that there is a minimum of contamination on the packaging that could be activated and produce unwanted activity.

This vial can then be sent to the core using the pneumatic transfer system. This pneumatic transfer system has several advantages. First it allows for the sample to be inserted and removed very quickly, which allows for accurate irradiation times. Also, the tube is not much larger than the vial so samples can be irradiated with a consistent geometry sample after sample.

After the sample is prepared and labeled it is then irradiated at 20 kW, or a thermal flux of  $1.86E11$  n/cm<sup>2</sup>/s, for the appropriate amount of time – 15 seconds for the Cadmium samples and 30 seconds for the gold samples. During all of the irradiations the shim rods of the reactor were kept as close as possible to 21.7 inches with the regulating rod being positioned where necessary to maintain criticality. Also, the power indication display on the picoammeter was kept as close to 10.26 as possible while the irradiation was taking place.

When the sample returned from the core and was determined safe to handle it was placed in an overpack, which also had a centering device designed for the rabbit vial. The overpack was used so that the contaminated sample could be handled and counted easily without spreading contamination.

The overpack was then placed on the detector, which has yet another centering device designed to keep the overpack centered on the detector. Then two minutes after the return of the sample the sample was counted for 10 minutes of live time. A live time count counts for extra time to make up for the amount of time the system misses counting

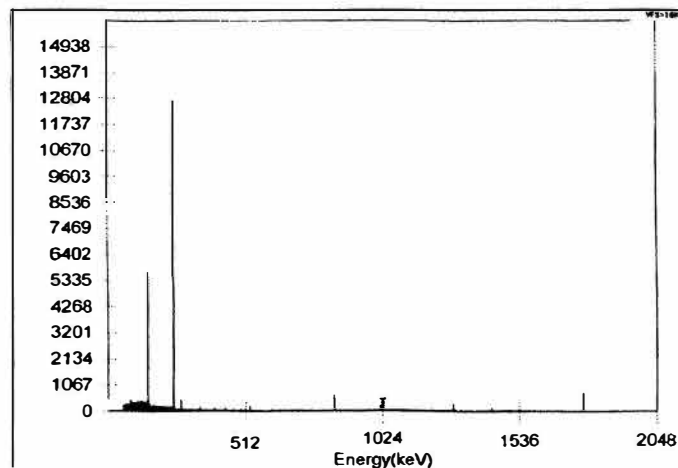


radiation because it is recovering from the last count. In a gamma spectroscopy system most of this time is taken by the multichannel analyzer to store the data in the appropriate channel. The dead time increases as the activity level of the sample increases. For samples that have a long half-life this approximation for making up for dead time is very accurate. The gold nuclide being measured has a half-life of about 2.7 days so the dead time is not even a consideration. The cadmium has a half-life of about 48.5 minutes so as long as the dead time correction is a small percentage of the counting time the error is small. When the count is completed the data is saved and the next sample can be irradiated.

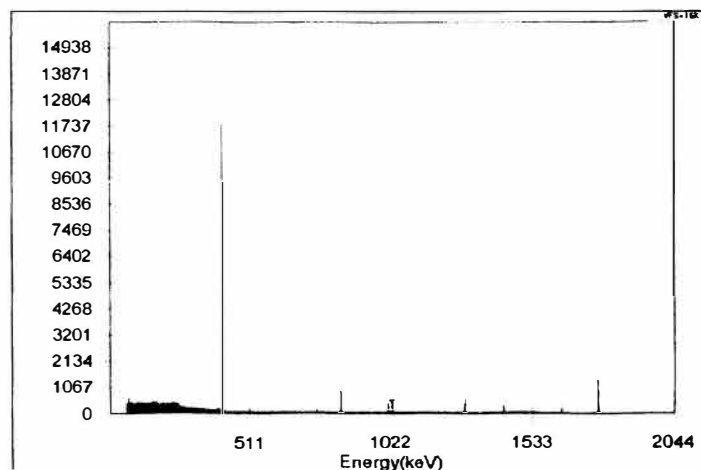
## Data and Observations

A typical gamma spectrum for the Cadmium is shown in Figure 3. The radioactive nuclide of cadmium that was measured is Cd-111m, which is a metastable isotope of Cadmium that has the same mass as the stable nuclide of Cd-111, but the nucleus has extra energy. The nucleus releases this extra energy in the form of gamma rays and then becomes the stable Cd-111 nuclide. This nuclide releases two prominent gamma rays. The first is at 150.81 keV with a probability of 30.9% and the second is at 245.39 keV with a probability of 94.0%. The second peak is more probable and therefore is used in all the calculations.<sup>3</sup>

A typical gamma spectrum for the Gold is shown in Figure 4. The radioactive gold nuclide that is being measured is Au-198. This isotope only has one prominent gamma ray and it has an energy of 411.8 keV with a probability of 95.5%. This nuclide eventually decays by beta minus emission into Hg-198, which is a stable isotope.



**Figure 3: A typical gamma spectrum for Cadmium. The two large peaks are both from the radioactive Cadmium isotope.**



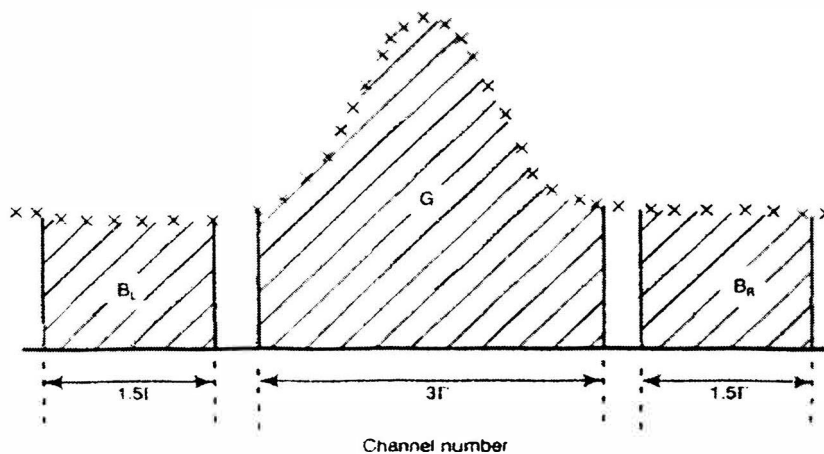
**Figure 4: A typical gamma spectrum for Gold. The large peak on the left is the peak for the radioactive gold isotope.**

The data is then reduced to a set of x-y data points of channel and counts. The following formula is then used to calculate the net peak area for the count. This formula sums the counts within three full widths at half maximum (FWHM) and then subtracts the counts at 1.5 times the FWHM (also denoted as  $\Gamma$ ) on either side of the peak. This removes the extra gross radiation from the peak that is not caused by the isotope of interest. This is also depicted in Figure 5<sup>1</sup>.

$$NPA = G - B_L - B_R \quad (\text{Eq. 4})$$

Where:

- $NPA$  = Net Peak Area
- $G$  = Gross counts within three times the FWHM
- $B_L$  = Background levels to the left of peak within 1.5 times FWHM
- $B_R$  = Background levels to the right of peak within 1.5 times FWHM



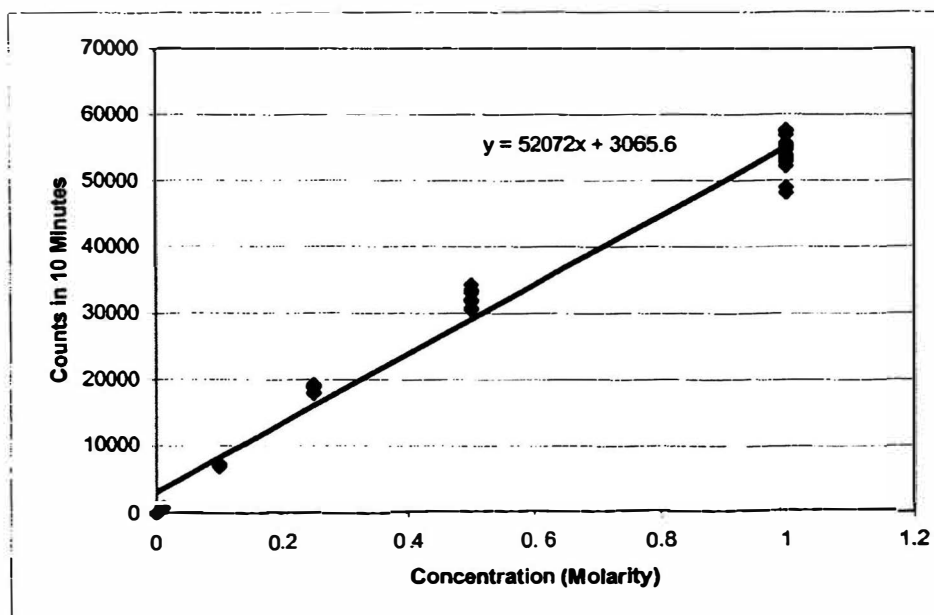
**Figure 5: Determination of the net area under the peak using Eq. 3.<sup>1</sup>**

At this point the regular background radiation when the sample is not present could also be subtracted out. However, the background level is so low because of excellent shielding that background without the sample was ignored. The background would only amount to 10 or less counts over a 10-minute period and when dealing with thousands of counts this level is negligible. Also, the background radiation spectrum is relatively flat without peaks so the net peak area calculation method takes care of the background.

After the net peak counts is calculated for each of the samples, then the data can be plotted and the standard deviation of each of the sample sets calculated. Table III shows the cadmium data and Figure 6 shows the plot of the cadmium data.

**Table III: CdNO<sub>3</sub> net peak areas.**

<b>Sample for Concentration</b>	<b>0.001 Molar</b>	<b>0.01 Molar</b>	<b>0.10 Molar</b>	<b>0.25 Molar</b>	<b>0.50 Molar</b>	<b>1.00 Molar</b>
1	38	759	6988	17880	31772	53886
2	18	722	7280	19183	30562	52871
3		708	6770	18798	33509	48176
4		723	7207	18944	30710	53684
5		772	7342	18013	33352	48956
6					33071	57653
7					33288	56936
8					32060	54801
9					30782	54957
10					34263	54868
11						53489
12						55072
13						52181
14						55327
15						57514
16						53215
17						55645
18						54689



**Figure 6: Cadmium data plotted for the various concentrations.**

From Table III and Figure 6 it can be seen that the standard deviation for the different sample sets is relatively low and this is shown in Table IV. The only concentration that has a high error is the 0.001 molar solutions and this is because there were only 2 samples done for this concentration and this is at the lower limit of the detection threshold for cadmium.

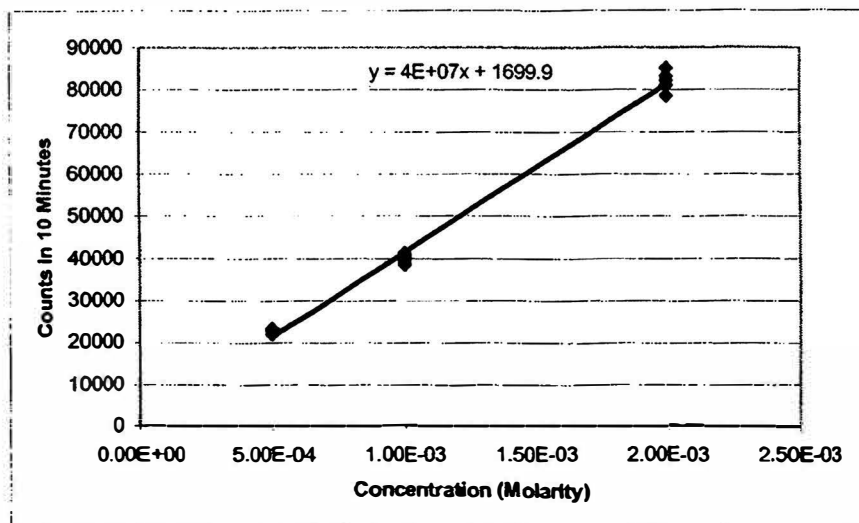
**Table IV: CdNO3 standard deviation data.**

	0.001 Molar	0.01 Molar	0.10 Molar	0.25 Molar	0.50 Molar	1.00 Molar
Standard Deviation	34.96%	3.31%	2.96%	2.80%	3.93%	4.65%

The same reduction was done for the data for the Gold solutions. However, two different chemical forms of gold were used – H<sub>2</sub>AuCl<sub>4</sub> and KAuCl<sub>4</sub>. These yielded different results and the reason for this is not yet known. Presumably, one of the sets of solutions was prepared incorrectly but it has not yet been determined which one was incorrectly prepared. Additional solutions will have to be prepared to determine which one is correct. The H<sub>2</sub>AuCl<sub>4</sub> data is shown in Table V plotted in Figure 7 and the KAuCl<sub>4</sub> data is in Table VII and plotted in Figure 8.

**Table V: H<sub>Au</sub>Cl<sub>4</sub> net peak areas.**

Sample for Concentration	5E-4 Molar	1E-3 Molar	2E-3 Molar
1	23209	39734	82175
2	22949	40358	81080
3	22170	39862	83198
4	23495	38860	78665
5	23521	41281	85040
6		40802	
7		38569	



**Figure 7: Gold data for H<sub>Au</sub>Cl<sub>4</sub> for various concentrations.**

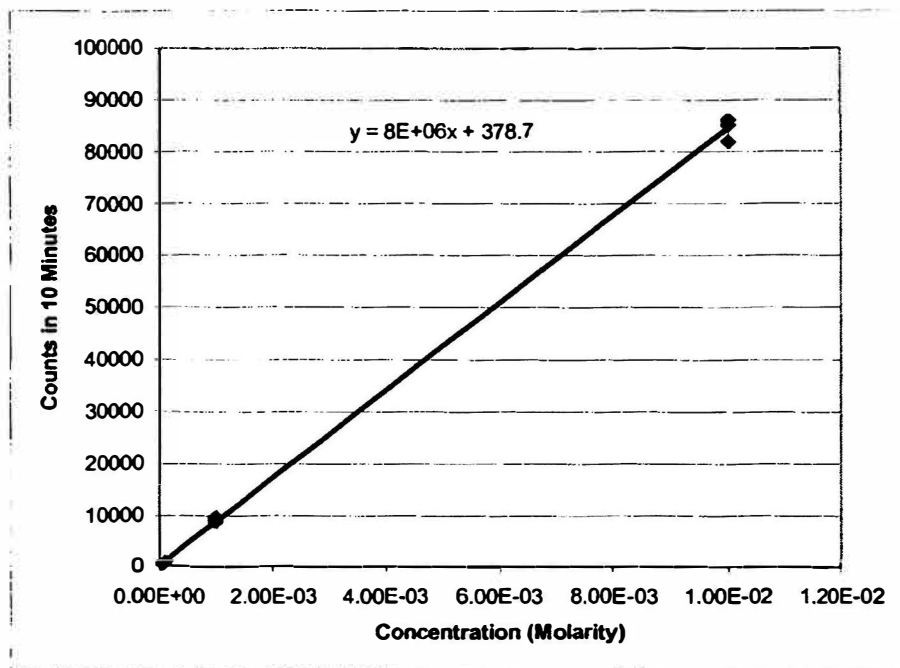
Again the standard deviation is quite small for the H<sub>Au</sub>Cl<sub>4</sub> samples and is shown in Table VI.

**Table VI: H<sub>Au</sub>Cl<sub>4</sub> standard deviation data.**

	5E-4 Molar	1E-3 Molar	2E-3 Molar
Standard Deviation	2.15%	2.28%	2.60%

**Table VII: K<sub>Au</sub>Cl<sub>4</sub> net peak areas.**

Sample for Concentration	5E-5 Molar	1E-4 Molar	1E-3 Molar	1E-2 Molar
1	483	1046	8998	81924
2	574	845	9790	85241
3	518	869	8849	86212
4	508	887	9592	
5	532		8953	
6			9479	



**Figure 8: Gold data for KAUCl4 for various concentrations.**

The standard deviation data for the different concentrations is shown in Table VIII.

**Table VIII: KAUCl4 standard deviation data.**

	5E-5 Molar	1E-4 Molar	1E-3 Molar	1E-2 Molar
Standard Deviation	5.76%	8.66%	3.86%	2.17%

The two gold solutions can also be plotted together to see the difference in the counts recorded for the same molarity.

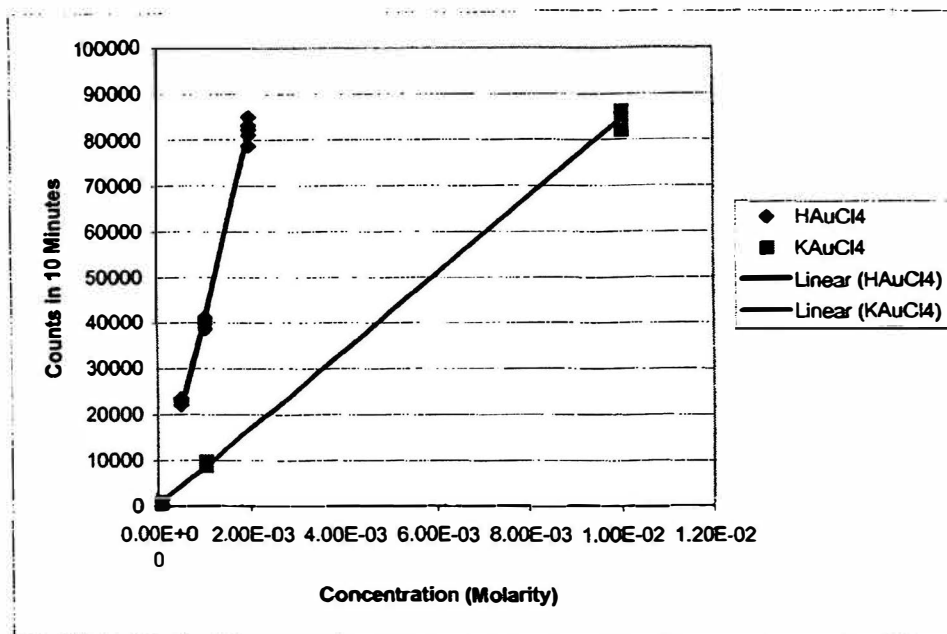


Figure 9: HAuCl<sub>4</sub> and KAuCl<sub>4</sub> data plotted together.

## Conclusions

The counts recorded for the Cadmium and the Gold were both linear. This was theoretically predicted since the irradiation time is short compared to the half-lives of the isotopes and because such a small number of the target nuclei are transmuted into radioisotopes.

This method of using NAA should be able to be used to determine amounts of these metals in other samples. A baseline can be established using these known solutions and from that an unknown solution's concentration should be able to be determined based on the number of counts recorded under the same circumstances as the known solutions.

## Acknowledgements

I would like to thank Dr. Massimo Bertino and Dr. Akira Tokuhiko for their guidance on this project and all of their help. Chuck Williams also deserves thanks for all of his help on collecting much of this data. Finally, I would like to thank the staff of the UMR reactor for operating for me for the many hours it took to gather all of this data.

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