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Recovery of Gold from Radioactive Gold Waste Using The Redox Replacement Method with Zn-Foil Reductor

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Abstract. The residual waste of synthesis and use of radioactive elements of gold ^{198}Au as a radiopharmaceutical and tracer after decaying can be reused as an irradiated target material. The gold recovery process was carried out on Au-198 radioactive nano gold waste with the redox replacement method using Zn-foil as metal reducing agent. Radioactive Au-gold waste was stored until it decayed to its background, so it is not dangerous and does not interfere with the optical characterization process. The sample was dissolved with aquaregia and evaporated so that the chelating or dendrimer material can be released and oxidized. The evaporation was done to reduce acidity and obtain the salt. Furthermore, the salt solution of HAuCl_4 is reduced with Zn-foil so that the pure gold deposits can be obtained through a redox process. The results of the XRF analysis showed that the gold deposits formed have fairly good purity with little Zn and Zr impurities derived from the erosion of the melting container. The yield calculation results based on ICP-OES data obtained a recovery percentage of 68.73%. The method of taking gold deposits must be increased to reduce the gold particles attached to the bar stirrer and to the melting pottery container.

Keywords: Recovery, ^{198}Au -Nanoparticles, Redox replacement

1. Introduction

The rapid development in nuclear medicine demands a variety of radionuclides for many purposes [1,2]. The production and utilization of radionuclide in nuclear medicine will produce a lot of radioactive waste derived from the synthesis of radiopharmaceutical materials and the excretion of these drugs from human body [3]. One of the radionuclide used in therapy and diagnosis is gold-98 (Au-198). Au-198 is an artificial radionuclide which has a short half-life of around 2.69 days. This radionuclide is produced using a target source of natural isotopes Au-197 which are activated into Au-198 and decayed into Hg-197 [4]. The irradiation process of gold makes it potential cancer therapy agent because it emits gamma energy at 412 KeV and Beta 1.0 Kev in its decay which can be used as a therapeutic and diagnostic agent simultaneously in nuclear medicine [5,6].

The synthesis of gold nanoparticles aims to obtain stable gold nanoparticles for parenteral use [7]. In general, the initial treatment of the synthesis of gold nanoparticles is to convert gold metal into a gold solution (III) Chloroauric acid, then gold is reduced slowly by keeping nanometer size of particles using dendrimer. Hosyar, et al had synthesized gold nanoparticles using dendrimer crocin and found a stable



and effective Au-NP-Crocin used as an agent for breast cancer therapy [8]. Ritawidya et al. have synthesized radiopharmaceutical $^{198}\text{AuNP-PAMAM-G3}$ from Au-198 in the form of $\text{H}^{198}\text{AuCl}_4$ with dendrimer Poly Amidoamin (PAMAM) for brachytherapy [9].

Gold nanoparticles that have been used as therapeutic and diagnostic agents will be excreted from the body through urine and produce dendrimer-coated gold nanoparticles in both active and inactive form. Chaterin et al. have investigated the using of gold nanoparticles as agents for breast cancer therapy and found that gold nanoparticles are excreted through urine in the form of stable AuNp-NCs along with several amino compounds [10]. Research on gold nanoparticles as a potential material for contrast agent compounds has been carried out by Adang et al. using distribution test and clearance test of $^{198}\text{AuNP-PAMAM-G4-NIMOTUZUMAB}$ as medicinal ingredients in mice. The results of distribution study showed that the compounds accumulated in the kidneys, liver, and spleen. Then the radioactive compound was excreted from the body of the rat through urine in the form of $^{198}\text{AUNP-PAMAM-G4-NIMOTUZUMAB}$ [11]. Gold in this form is still stable at the nanometer size until there is a separation of dendrimers from gold by physical, chemical and biological treatments.

The abundant gold content in the waste after the synthesize process of Au-198 and its radiopharmaceuticals is a reason for the recovery of gold. Zhang, et al. had performed gold recovery using the ion exchange method using a solution of Iodine and Iodide as a reducing agent for the solution of gold chloroauric acid (HAuCl_4). The better recovery results had been obtained by adding sulfite ions in the iodide solution [12]. The disadvantage of using Iodide as a reducing agent is its volatiles due to acid or heat thereby reducing the percentage of redox reactions.

In this study, it was reported the process of recovery of gold from radioactive nanoparticles synthesized Au-198 gold waste using the redox replacement method with Zn-foil as reducing agent. The use of metal and non-volatile Zn-foil reducing agents is an easy way to recover gold from the HAuCl_4 gold solution, allowing an increase in the percentage of redox replacements [13]. The determination of gold content in the waste was carried out using the ICP-OES and qualitative testing of recovery results of solid gold using XRF.

2. Materials and Method

2.1. Materials

The gold solution of Auric acid HAuCl_4 was taken from the remaining inactive HAuCl_4 waste from the laboratory of Center for Radioisotope and Radiopharmaceutical Technology, National Nuclear Energy Agency (BATAN). Zinc foil (99.99%) was purchased from Merck, and Aquadest was obtained from self-production by PTRR.

2.2. Preparation of samples from radioactive gold waste.

The first step in the recovery process is the HAuCl_4 waste solution piped as much as 250 mL from the CRRT, NNEA's laboratory and radioactivity level testing using a gamma spectrometer (HPGe). Gold waste with the background activity level was then added a solution of aqua regia acid for the chelate oxidation, then it was evaporated until a salt was formed and re-dissolved with distilled water. Furthermore, the sample solution HAuCl_4 was tested by ICP-OES to determine the concentration of gold in the solution.

2.3. Gold recovery process

The sample solution of 100 mL of Auric Acid waste was mixed with a reducing agent of pure zinc 40 mg form Zn-foil for reducing the gold. Then the solution was stirrer approximately 2 hours until the solution was clear and the gold deposits were separated from the filtrate by the decantation method. This process was carried out on three samples to obtain comparative data.

The deposits of gold were then washed with distilled water 5 times to be free of impurities, then the gold powder was dried, weighed and calculated as the percentage of recovery. The powder obtained was heated in the furnace at a temperature of 1100°C , then the melted gold poured into water to form solid

gold. The solid gold was then characterized using the XRF device to determine the presence of impurities contained.

3. Results and Discussion

The radioactive that is still high from a radioactive waste can be a barrier on carrying out the recovery process. Therefore, the emission of radiation from the sample solution is measured using a gamma spectrometer to determine the level of activity and types of radionuclides contained in waste [14,15]. In order to see that radioactive substances from the waste have been safely used, the results are compared to the pattern of gamma radiation spectrum of background shown in Figure 1.

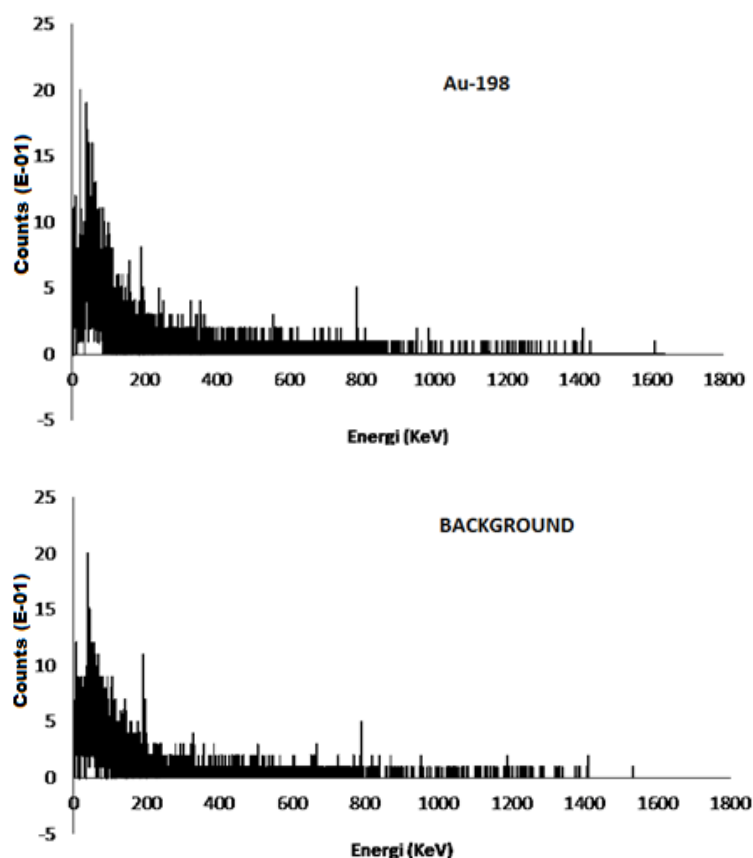
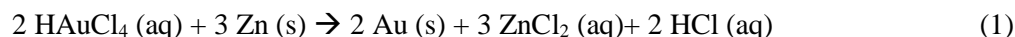


Figure 1. Comparison of results of Au-198 (top) gamma spectrum pattern with background (bottom).

Figure 1 shows that there is no radioactivity indicated by the absence of the peak of the golden isotope Au-198 in the 412 KeV gamma energy. This indicates that the gold radioactivity was too low to interfere with the characterization of the sample. the low gamma radioactivity indicates a safe condition and will not harm workers in conducting the research process [16,17].

The content level of gold metal in waste needs to be analyzed to the smallest concentration to get the actual concentration of gold so that the efficiency of the method of recovery can be determined. Measurement of metal content in the sample was carried out using an ICP-OES which can detect substances up to nanometer size [18,19]. From the results of ICP-OES analysis of 250 mL of HAuCl_4 samples, the gold concentration was 493.575 mg / L. The gold waste sample was clear and yellowish which indicates that the sample solution was homogeneous, so it is possible to know the concentration of gold from the sample trailer correctly. In this way, we can also estimate the total amount of gold formed.

The reaction that occurred in the gold recovery process was a reduction-oxidation reaction based on equation 1, wherein the zinc metal was oxidized to Zinc (II) ion and gold (III) being reduced to metallic gold (0). This is caused by the zinc metal has a reduction potential $E^\circ = -0.7618 \text{ eV}$, so that it is easily oxidized, and the reduction potential of gold $E^\circ = +0.93 \text{ eV}$ so is easily to reduced.



The reaction can be observed through discoloration of the solution from yellow to clear accompanied by the formation of gold deposits as shown in Figure 2.

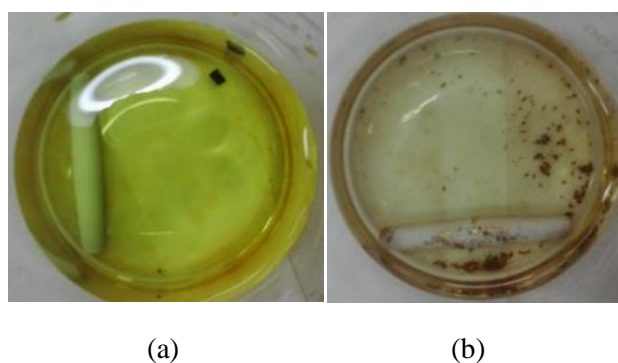


Figure 2. Change of color of HAuCl_4 (a) solution after the reduction process with Zn-foil metal becomes transparent and there is gold deposits (b)

Table 1. the results of solid gold

Sampel	HAuCl_4 (mL)	Zn (s) (mg)	Yields of Au (s) (mg)
A	100	40	29.97
B	100	40	34.00
C	100	40	37.80
Total	300	120	101.77

In table 1, the result of recovering gold from waste using zinc metal reducing agents is presented. In the electrochemical calculation the amount of zinc elements used is more than the gold element so that the redox exchange reaction runs perfectly. The difference in gold recovery results might caused by the presence of fine gold granules which are still attached to the bar stirrer. This indicates that the steering bar has quite large pores and can cause gold nanoparticles to enter the pores. Therefore, during the recovery process, equipment which has very small pores must be used. The calculation of yields of recovered gold can be seen through the calculation below:

$$\% \text{ yield} = 101.77 \text{ mg} / 300 \text{ mL} \times 1000 \text{ mL} / 1\text{L} \times 1\text{L} / 493,58 \text{ mg} \times 100\% = 68.73\% \quad (2)$$

The yield percentage of 68.73% indicates that the value of process efficiency is still low. For this reason, it is necessary to develop gold sample recovery techniques.

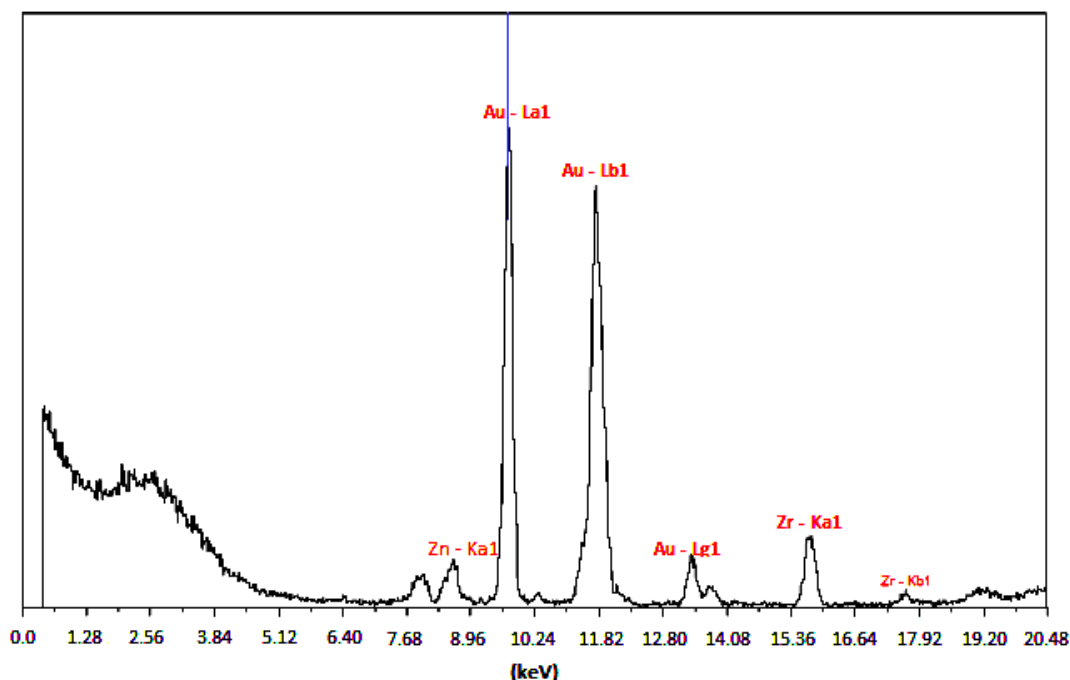


Figure 3. XRF graph of gold solid samples at an energy peak of 9.7 KeV; 11.01 KeV; and 13.44 keV.

The gold content needs to know as best as possible to find out the purity of gold, the impurities that follow and the source of origin of impurities that may be obtained during the recovery process. Characterization instrument which has good accuracy is XRF which uses the principle of X-ray fluorescence comparison after passing through the sample. The results of XRF analysis of the gold metal obtained can be seen in Figure 3 [20]. In the picture, the XRF pattern has the highest peak intensity at 9.7 keV which shows the intensity of the gold elements.

The peak of La1, Lb1, and Lg1 indicates the characteristics of X-rays emitted by the gold element when shot by high-energy photons. Photons will excite their inner electrons on the L orbital or the second layer but not excite the electrons on the deepest orbital, namely the K orbital and emit x-rays with lower energy. This is because gold is a transition metal element with a large atomic number, a radius of a larger atom and has the outermost layer of orbital to f [20].

The zinc peak which comes from the filtrate is the result of the recovery process which is not lost during the washing process so that more washing needs to be done. Emerging zirconium element peaks indicates zirconium impurities at yield. Zirconium was derived from the erosion of a pottery container used as a melting point for gold metal. For the better process, melting containers are needed with materials that are more heat resistant and not easily eroded.

4. Conclusion

The recovery of gold from radioactive AuNP waste can be done by using the Zn metal reducing agent. The recovery result was 68.73% which indicates that the recovery process is not optimal due to the presence of gold metal attached to the magnetic rod used to stir the solution during the recovery process. Based on the experiments, good results were obtained in the 3rd experiment where the gold recovery concentration was 37.80 mg Au metal using 40 mg of zinc metal reducing agent. The results of XRF characterization shows that there are few impurities Zn, and Zr which come from the melting container.

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