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The analysis of gold in seawater using ion exchange chromatography and atomic absorption spectroscopy

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THE ANALYSIS OF GOLD IN SEAWATER USING ION EXCHANGE CHROMATOGRAPHY AND ATOMIC ABSORPTION SPECTROSCOPY

by

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THE ANALYSIS OF GOLD IN SEAWATER USING ION EXCHANGE CHROMATOGRAPHY AND ATOMIC ABSORPTION SPECTROSCOPY

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This thesis was prepared under the direction of the candidate’s thesis advisor, Dr. Eugene Smith and has been approved by the members of his supervisory committee. It was submitted to the faculty of The Honors College and was accepted in partial fulfillment of the requirements for the degree of Bachelor of Arts in Liberal Arts and Sciences.

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Gold is a highly prized metal whose ore deposits are continually being mined and depleted. With the increasing scarcity of continental gold ores, gold miners and scientist are turning to the sea as one alternate source of this precious metal. But the problem arises in determining which parts of the ocean to mine. Ideally the area with the greatest concentration of gold would be the best place to start but determining an accurate concentration of gold in a sample of seawater is difficult for various reasons. The main reason being gold’s extremely low concentration in seawater, averaging at about 13 parts per trillion. This study deals with detecting trace amounts of gold in seawater. The first step in the analysis involves pre-concentrating gold in seawater using an ion exchange resin, Chelex® -100, and optimizing the experimental conditions. Then the chromatographic fractions are analyzed using a graphite furnace atomic absorption spectrometer. The results from several trials are presented in this study.
“TO MY PEOPLES”
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Introduction

Gold has long been considered a precious element throughout history and societies. It has been sought after in every corner of the world by many different people of different professions. Alchemy, turning base metals into gold, was considered a serious subject up until the 16th century and even as recently as 1995 some professors were researching the idea of turning lead into gold (Newsweek, 54).

Much of the gold that has been mined as of today has been from rocks, rivers and stream beds. As these sources become depleted, miners are looking for new sources - including the sea. The gold in seawater comes from many different places: gold ores in the ocean strata, gold-carrying rivers and streams flowing into the sea, sediments of gold imbedded in the sand and gravel of beaches, and sulfide gold deposits formed by hydrothermal vents (McNulty).

Analyzing gold in seawater is a challenge due to its dilute concentration and other species in seawater that could interfere with analysis. Nevertheless, seawater contains about 25 billion ounces of gold, but because of the enormity of the sea, the gold is diluted from 5 to 50 parts per billion (ppb), that amounts to 1 gram of gold for approximately every 200 tons of seawater. Even so, the sea has become a newly sought after avenue for mining gold, but many obstacles hamper it from becoming an economically viable source (McNulty).

One example of an attempt to isolate gold from seawater was in 1920 when a scientist named Fritz Haber tried to help Germany pay off the reparations debt imposed on it due to World War I. His endeavors failed because he realized that there was simply not enough gold present in seawater and therefore it would not be cost-effective, but he
did figure out a precise method for measuring the concentration of gold in seawater (World of Chemistry).

Another example dealing with the detection of small amounts of gold is found on the island of Sardinia (located west of Italy) where scientists are trying to develop a method for determining the concentration of gold in various media. Rocks, called andesite, which are associated with gold, were discovered on the island. If andesites are found in large amounts it would be enough to justify commercially mining the area. Traditionally, samples of rocks, soils and stream sediments had been analyzed to determine gold amounts and thus potential sites to mine. But scientists also realized that analysis of water from nearby streams would be just as helpful in determining trace gold amounts (Innovations, 3).

The method that was developed by the University of Cagliari to analyze the water samples was the use of an ion-exchange resin, such as Chelex®-100, to concentrate the sample followed by analysis with graphite-furnace atomic absorption spectroscopy (GF-AAS). The reason for carrying out preconcentrations of the sample with an ion-exchange resin is because simply using GF-AAS is insufficient in detecting gold among all the other salts present in seawater. Also, chelating resins have been widely used as an aid to speciation of very low concentrations of metals in natural waters and has a well-known and established utility in column filtration (Mora et al., 307). The results of this method agreed with other methods including traditional methods and were helpful in locating potential mining sites in Sardinia. The success of ion-exchange resin coupled with GF-AAS analysis leads to the use of it in analyzing gold particles in other sources, particularly seawater (Innovations, 4).
Chelex®-100, specifically, has been found to have a relatively high binding capacity for gold (III) when compared to other resins (Koshima, 255). Figure 1 shows the structure of the chelating ion exchange resin which is composed of styrene divinylbenzene copolymers and iminodiacetate ions that act as cation or anion exchanger based on the pH of the mobile phase. Chelex®-100 is selective for bi- and trivalent ions over monovalent ions by a factor of approximately 5,000 to 1. When the resin is in a fairly basic solution it becomes fully deprotonated and develops a triple binding site which allows it to bind to the trivalent gold (III) ion.

Figure 1. Styrene copolymer (left) and iminodiacetate ions (right) binding to bivalent metal, X is where the iminodiacetate ion bonds and R-group represents styrene copolymer. University of Helsinki-http://ethesis.helsinki.fi/julkaisut/mat/kemia/vk/leinonen/3luku.html

Because of gold’s extreme dilution in seawater it is very difficult to treat it in seawater solutions and experimentally analyze for it. As a result, pretreatment procedures have to make use of reagents that have a high affinity for gold and form stable complexes. The purpose of this study is to test the particular aforementioned method of using Chelex®-100 as a viable reagent in analyzing trace gold particles from seawater. This will be done by concentrating gold in a seawater solution and measuring the amount of gold present by GF-AAS.
Experimental Methods:

Pretreatment Method:

A standard filtration column with the chelating resin Chelex® -100 Biotechnology Grade as the stationary phase was used. The chelating resin solution was prepared by dissolving 10 grams of the resin in 200 mL of distilled water and pouring the solution into a 34x2cm column such that there resulted in a five (5) centimeter thick resin at the bottom of the column. Afterward the column was equilibrated by running a series of acidic and basic solutions through it. First, 200 ml of 1M hydrochloric acid (HCl), followed by 400 ml of distilled water was allowed to run by gravity. Second, 200 ml of 1M sodium hydroxide (NaOH) was added immediately after and was also allowed to run by gravity. At this step the prepared seawater/gold sample was introduced. Two separate preconcentration steps were done using different gold sample concentrations; these are discussed in the next section. In each of the preconcentration steps the pretreatment of the column was identical.

First Preconcentration

After the calibration period, a 100 ml gold sample of 13ppb, which was prepared by diluting 100 µL of a 1g/L standard solution of gold to 100 ml, was added to the column and collected in 20 ml fractions using gravity filtration. Five samples were collected and analyzed by GF-AAS.
Second Preconcentration

Fresh chelex resin was used but the thickness of the resin bed in the column was kept the same. After the equilibration pretreatment process, a 250 ml 1ppm gold sample, which was prepared by diluting 250 µL of a 1g/L standard solution of gold to 250 ml, was added to the column and collected in 2 ml fractions using a Spectra/Chrom® MP-1 Pump and Spectra/Chrom® CF-1 Fraction Collector.

This allowed for the collection of approximately 2 ml of sample per test tube at approximately 2 ml per minute (5 rpm pump setting). 125 samples were collected but only every fifth sample was analyzed. This gave a total of 25 test tubes with 2 ml of sample each.

Spectroscopic Analysis

When electromagnetic radiation in the form of light interacts with matter, excitation of valence electrons occurs. The energy emitted and absorbed is proportional to the frequency (ν) of light transmitted by the following equation, where h is Planck’s constant:

\[ E = hv \]

Atomic spectrometry deals with ultraviolet, visible and infrared light typically of wavelength between 180 and 900nm. Different elements absorb at different wavelength, gold, specifically, transitions at approximately 242.8nm.

Atomic emission occurring in the light source of a spectrophotometer involves atoms emitting photons in the form of light after being excited by a transfer of energy in
the form of heat. The energy in the emitted photons is equal to the difference in the ground state and excited state of the atom.

All samples generated in the experimentation were analyzed by atomic absorption spectroscopy; specifically, graphite furnace atomic absorption, a diagram of which can be seen in Figure 2 below.

![Graphite furnace atomic absorption spectrophotometer diagram](<www.kntc.re.kr/.../nuclearfeul_13/ch13_4.html>)

**Figure 2. Graphite furnace atomic absorption spectrophotometer.**

This involves a hollow cathode lamp (HCL) which is used as the source, a monochrometer, a graphite tube as the atom cell in which the sample is injected, and a photomultiplier as detector. A discrete amount (20 µL) of the sample is injected in the graphite tube which is heated by the furnace at a series of temperatures for specified times. This is called the atomization cycle where the final atomization step reaches temperatures of 2300° C and converts the entire sample into gaseous atoms. A cleanout temperature of 2400° C was used in this experimentation.
A graphical representation of the temperature program used is shown in Figure 3 and a general mechanism for the charring process is described as follows:

Metal salt (aq) → metal salt (s) → metal oxide (s) → metal (s) ↔ metal (g)

(Butcher et al., 19)

---

![Temperature Program](image)

**Figure 3. Temperature program used in analysis**

At the point where the gold solution becomes gaseous metal ions, absorption can effectively occur. Absorption involves the transfer of energy from a photon to a gold atom to promote a valence electron in the atom from the ground to the excited state. For absorption to occur, the energy of the photon must be identical to the difference in energy between the lower and higher energy levels of the atom, i.e., gold (Butcher et al., 5).

A Perkin Elmer atomic absorption spectrometer model 5100 Zeeman, and furnace model HGA-600 were used to analyze both preconcentration samples. Different machines were used for each preconcentration sample due to some mechanical
complication with the first machine after the first analysis. In each case, the experimental parameters were a wavelength of 242.8nm, slit of 0.70mm and energy of 27 and 48 mA for each analysis, respectively. A calibration curve was developed by analyzing standard solutions of gold using GF-AAS. Four standard solutions of gold were prepared: 10ppb, 20ppb, 30ppb and 50ppb. The same standards solutions were used for the analysis of both preconcentration samples, although the standards were passed through the GF-AAS separately before both analyses.
Results and Discussion

First preconcentration

A calibration curve was developed with the standards using an Excel spreadsheet the results are shown in Figure 4. The standard curve yielded an $R^2$ value of 0.957. The curve was used to determine the concentrations of the five samples. The samples are plotted in Figure 2. As expected, the concentration of gold increased with each successive fraction/sample. The total amount of gold collected from all fractions was 0.00394mg. The percent recovery was 303.1% (0.00394 mg gold recovered / 0.0013 mg gold added) because only 0.0013 mg of gold was added to the seawater sample, this suggests that interferences influenced the analysis.

![Figure 4. Standard curve for first preconcentration](image-url)
Figure 5. Amount of gold in each fraction for the first preconcentration

The result of the first preconcentration analysis (see Table 1) showed a need to increase the number of samples collected. Therefore, the number of samples collected was increased from 5 to 125 in the second preconcentration and only every fifth sample was analyzed for a total of 25 samples. This was done to decrease the duration of the analysis process and still maintain high precision, analyzing 125 samples via GF-AAS would simply be too exhaustive.

<table>
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<th>mL</th>
<th>ppb Au</th>
<th>mg Au</th>
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</table>

Table 1. First preconcentration results
Second preconcentration

An $R^2$ value of .975 was observed for the standard calibration curve of this preconcentrated sample. This correlation is shown graphically in Figure 6. A percent recovery of 2.46% was obtained. A graph of the chromatographic fractions and the amount of gold detected in each is shown in Figure 7. Fractions that yielded negative values were graphed as zero. The precise numbers are organized in Table 2.

Some key differences in the analyses might give some insight into the dramatic differences in percent recoveries. First the second analysis had a longer period between the preconcentration step and the actual analysis by GFAAS. This longer period could have allowed the gold in the samples to precipitate out of solution, and salts to crystallize. Second, because a different GFAAS machine was used for the second step the sensitivity for gold might have been different, although this is very unlikely. Also, analyzing only every fifth sample could have contributed to the low yield in the second analysis, that is, the unanalyzed samples could have contained a higher concentration of gold than the analyzed samples.

Changing the pretreatment step in such a way as to minimize interference by decreasing the amount of salts in the sample could be one possible avenue for future experimentation. Varying the equilibration method of the column to make it more selective for gold might also help in obtaining better results.

\*Actual amount of gold detected is 0.000821mg of gold*(5ml/1ml)*(3ml/2ml) mg. The amount of gold detected is multiplied by factor 5ml/1ml because only every fifth sample was analyzed out of the 125 samples. A another factor of 1.5ml is used because the 2ml samples were diluted with 1ml of distilled water prior to analyze due to some samples drying out.
Figure 6. Standard curve for second preconcentration

Figure 7. Amount of gold in each collection fraction for the second preconcentration
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<tr>
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</tr>
</tbody>
</table>

Table 2. Second concentration results, actual total is obtained by multiplying total by 5 since only every 5th fraction was analyzed.
Conclusion

The difficulty of the experiment is to be considered with the results. Determining exact or near exact concentrations of any element or compound known to be in the parts per billion or lower in seawater requires a precise and methodical process. The analysis of gold in seawater using ion exchange chromatography and graphite furnace atomic absorption spectroscopy proves to be reliable and is a feasible method to determine minute concentrations of gold in seawater but it does need to be perfected. Also, although the results obtained in this experiment were not conclusive, it did reveal a need for a more accurate method for pre-concentrating gold such as standard additions. Additionally, a better column pretreatment would be necessary before the elution of gold from the seawater sample.
References


Koshima, H (1986). Adsorption of Iron(III), Gold(III), Gallium(III), Thallium(III) and Antimony(V) on Amberlite XAD and Chelex 100 Resins for Hydrochloric Acid Solution. Analytical Sciences, 2, 255-260.

