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ORIGINALE ARTICLE

ANALYSIS OF ALBIZIA LEBBECK, FLACOURTIA RAMONTCHI, ANNONA SENEGALENSIS, AND IMPERATA CYLINDRICA USING DISPERSIVE ENERGY X-RAY FLUORESCENCE ANALYSIS TECHNIQUE FOR AURIFEROUS PROSPECTING IN THE RURAL MUNICIPALITY OF BETSIAKA

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ABSTRACT

Background: The discovery of gold in Madagascar is believed to have occurred in 1845, but significant mining operations did not commence until 1883. During the colonial era, various mining centers were established and contributed to gold production. However, following the country's independence, there was a sharp decline, with gold production reaching only ten kilograms in 1960. Since then, artisanal gold panning has become the primary source of gold production. Despite these historical developments, there remains a lack of comprehensive scientific knowledge to effectively identify the most promising gold deposits. Additionally, the high cost of advanced equipment restricts access for average gold miners. **Objective**: The objective of this study is to determine the quantity of gold present in the selected plant samples and explore potential methods for exploiting the gold sector in the Ambilobe District. **Method**: Samples were collected from the DIANA region in the northern part of Madagascar, specifically from the rural commune of Betsiaka, which falls within the Ambilobe District. The samples were subjected to analysis using the "Amptek EXP-2" Dispersive Energy X-ray Fluorescence (ED-XRF) method at the Laboratory of Nuclear Physics and Environmental Physics (LPNPE) at the University of Antananarivo, Madagascar. **Results**: The analysis of the plant samples revealed the presence of elements such as iron, copper, zinc, and gold. The levels of these elements varied depending on the sampling location and the specific part of the plant being analyzed. **Conclusion**: The analysis demonstrated that trace amounts of gold are present in some of the analyzed plant roots. However, the concentration of gold is minimal.

Keywords: Plants, XRF spectroscopy, Gold, Gold deposit and Mineralogy.

1. INTRODUCTION

The Malagasy subsoil holds significant potential in mineral resources, which are essential for the country's economic development. The island boasts a diverse range of mineral substances, including precious stones like sapphire and ruby, energy resources such as coal and hydrocarbons, as well as precious metals like silver, gold, and copper [1]. In this study, we focus specifically on gold exploration in the "Betsiaka" area, located east of the Ambilobe district in the Diana region of Madagascar. Our exploration efforts encompassed various gold sources, including confluence or mouth of effluent areas, inner curvatures of rivers, slope break areas (flattening after a considerable slope) in the flow bed, cracks, and even different plant specimens [2].

Several studies have been conducted on the scientific and technical analysis of gold characteristics. For instance, research has explored the environmental impacts of gold exploration in the "Maevatanana zone - III" project in the Maevatanana district of the Betsiboka region [3]. Additionally, magnetic prospecting of the gold deposit in the Iharanandriana region of the Vakinankaratra District and the multidisciplinary analysis of gold mineralization in the Maevatanana mining district have been investigated [4,5]. There is also a study on the geochemical exploration of primary gold in the northwest sector of Ambondrona Tsinjoarivo region - Ambatolampy [6]. However, from a scientific standpoint, the information available is still insufficient for accurately locating the most promising gold deposits. The high cost of advanced equipment makes it inaccessible to average gold miners, creating unfair competition among goldsmiths due to the difficulty in detecting exploitable areas without adequate resources.

Fortunately, we now have powerful tools for large-scale observations with detailed capabilities, which we aim to utilize in a more comprehensive approach to expand our investigative field and achieve more precise and fruitful results. Hence, we have chosen the theme of this research: "Analysis of plants by XRF spectroscopy for gold exploration." The results of our study will serve as a guide for prospecting and provide the necessary data for gold mining, which is the primary objective of our investigation in nuclear physics.

The following are the biological characteristics and analyzed parts of the plants studied:

> Albizia lebbeck:

Albizia lebbeck is a tree that can reach a height of 18 to 30 meters. The alternate, oval, elongated leaves are bipinnate, with leaflets that close to each other [7].







- Family: Fabaceae
- Scientific name: Albizia lebbeck
- Vernacular names: Bonara, Bonarabe, alibizara, black wood, oriental cabinetmaker, mother-in-law's tongue, fry-wood, lebbeck-tree, tongue tree, woman's.
- Analyzed parts: Leaf, Stem, and Root.

The figure presents shows Albizia lebbeck during the sampling.



Figure 1: Albizia lebbeck.

> Flacourtia Ramontchi

This thorny and bushy shrub can reach 10 to 15 meters high. Its single or forked spines disappear with age. Its branches have a yellowish grey to brown bark, cracked and scaly. Its leaves vary from elliptic to ovals, with or without acumen, glabrous or pubescent.

- Scientific name: Flacourtia indica,
- Family : Salicaceae,
- Vernacular names: Lamonty, valamoty, voandamoty, voatronaka, Malagasy plum, batoko plum, ramontchi.
- Part analyzed: Root, Stem and Leaf.

Figure 2 shows Flacourtia indica during the sampling.



Figure 2: Flacourtia indica.

> Annona senegalensis

Annona senegalensis is a species of trees or shrubs from semi-arid regions.

- Family : Annonaceae
- Vernacular names: kolopetaka, koropetaka, Senegalese cinnamon apple, apple custard, wild soursop.
- Part analyzed: Root, Stem and Leaf.
 Figure 3 shows Annona senegalensis during the sampling.



Figure 3: Annona senegalensis.



> Imperata cylindrica

It is a perennial, rhizomatous, monoecious herbaceous plant that can reach 1.5 m tall.

- Scientific name: Imperata cylindrica
- Vernaculars name: maneviky, antsoro, bozaka, fehena, manevika, tenina, tenona, baron rouge, *impérata cylindrica*, paille de dys, paillotte, blady grass, cogon grass, japonese blue grass.
- Part analyzed: Racine.
 Figure 4 shows *Imperata cylindrica* during the sampling.



Figure 4: Imperata cylindrica.

2. MATERIALS and METHODS

2.1 Sampling Strategy

The sampling strategy employed in this study was based on a probabilistic method using purely random sampling. Four different sampling locations within the rural municipality of Betsiaka, specifically fokontany Mantaly Maro, fokontany Andrafialava, fokontany Ankaramy, and fokontany Ambilo, were selected for investigation in the Ambilobe District. The objective of this work was to determine the target elements present in these plants. Dispersive energy X-ray fluorescence spectrometry was utilized as the analytical technique to determine the elemental content in different parts of the plants, including leaves, stems, and roots.

2.2 Sample Preparation

Sample preparation was initiated at 13:45 am on June 16, 2023, in the laboratory preparation room. Various materials were employed to transform the samples into a deposited form on the reflector. The following steps were performed:

Drying: The samples were dried for 24 hours at a temperature of 85°C in an electric oven.

Grinding: The dried samples were ground into powder using a grinder.

Sieving: The powdered samples were sieved to ensure uniformity.

Weighing: Precision balances were used to weigh the samples. Each pellet was prepared with a weight of 2 g and encoded accordingly.

The prepared samples included:

- Twenty-eight (28) samples of the plants studied from Mantaly Maro.
- Twenty-nine (29) samples of the plants studied from Andrafialava.
- Twenty-one (21) samples of the studied plants from Ankaramy.
- Twenty-two (22) samples of the plants studied from Ambilo.

2.2 Equation

The thick sample is frequently analysed with direct excitation X-ray fluorescence because the incident radiation absorbed by the sample is maximum and can result in the emission of optimal characteristic lines of excited elements in the analyzed sample. A sample is of intermediate thickness when:

0,1 <aipd< 1 (1)

With:

pd: the mass per unit area of the uniform thickness.

2.3 Analysis

The Department of Physics at the University of Antananarivo, Madagascar, possesses a qualitative and quantitative Xray fluorescence spectrometer for analyzing the elements present in the samples.



The laboratory's Nuclear and Environmental Physics section houses this spectrometer, as depicted in the figure below.



Figure 5: LPNPE X-ray Fluorescence Spectrometer.

The measurement conditions are:

- Counting time: 100 seconds;
- Tube voltage: 45 kV;
- Tube current: 10 µA.

Figure 6 shows the diagram of this analysis chain.

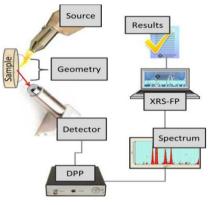


Figure 6: XRF chain diagram.

3. RESULTS

Tables 1, 2, 3 and 4 represent the mean (n=5) levels of the chemical elements in the samples from Mantaly Maro, Andrafialava, Ankaramy and Ambilo analyzed.

> Average sample concentration **from Mantaly Maro.**

Overall, the data suggests variations in the concentrations of different elements (iron, copper, zinc, and gold) among the analyzed plant species and their parts. The roots generally exhibited higher concentrations of iron, copper, and zinc compared to stems and sheets. These findings highlight the potential differences in element accumulation and distribution within different plant species and parts, which may have implications for their ecological roles and potential uses in various applications.

Table1: Change in concentration (mean ± SD) of elements in the analyzed samples from Mantaly Maro.

Element	Parts analysed	Albizia lebbeck	Flacourtia Ramontchi	Annona senegalensis	Imperata cylindrica
Tren	Sheet	10235 ± 20.14	6659± 48.87	6587 ± 56.90	
Iron	Stems	10354 ± 21.54	7415 ± 23.5	7003 ± 45.12	
mg/kg	Roots	11235 ± 41.89	9658 ± 39.65	9365 ± 69.32	12365 ± 79.8
Common	Sheet	738 ± 32.56	745 ± 16.58	886 ± 48.8	
Copper ma/ka	Stems	865± 10.24	895 ± 31.02	987± 39.14	
mg/kg	Roots	982 ± 56.47	963 ± 47.55	1023 ± 66.41	654 ± 22.9
Zinc	Sheet	8321 ± 41.02	9874 ± 74.32	13002 ± 61.03	
mg/kg	Stems	9324 ± 32.10	10248 ± 23.65	14025 ± 96.56	
	Roots	10235 ± 46.21	12054 ± 55.21	15874 ± 42.3	1984 ± 56.61
Cold	Sheet	<ld< th=""><th><ld< th=""><th><ld< th=""><th><ld< th=""></ld<></th></ld<></th></ld<></th></ld<>	<ld< th=""><th><ld< th=""><th><ld< th=""></ld<></th></ld<></th></ld<>	<ld< th=""><th><ld< th=""></ld<></th></ld<>	<ld< th=""></ld<>
Gold	Stems	<ld< td=""><td><ld< td=""><td><ld< td=""><td><ld< td=""></ld<></td></ld<></td></ld<></td></ld<>	<ld< td=""><td><ld< td=""><td><ld< td=""></ld<></td></ld<></td></ld<>	<ld< td=""><td><ld< td=""></ld<></td></ld<>	<ld< td=""></ld<>
µg/kg	Roots	5.3 ± 0.5	<ld< td=""><td>7.8 ± 0.4</td><td><ld< td=""></ld<></td></ld<>	7.8 ± 0.4	<ld< td=""></ld<>



> Average sample concentration from Andrafialava

Overall, the data indicates variations in the concentrations of different elements (iron, copper, zinc, and gold) among the analyzed plant species from Andrafialava. The roots generally exhibited higher concentrations of iron, copper, and zinc compared to stems and sheets. These findings highlight the potential differences in element accumulation and distribution within different plant species and parts, which may have implications for their ecological roles and potential applications.

Element	Parts analysed	Albizia lebbeck	Flacourtia Ramontchi	Annona senegalensis	Imperata cylindrica
Iron	Sheet	12547 ± 23.14	10235 ± 55.6	7894 ± 20.01	
mg/kg	Stems	13569 ± 25.87	10986 ± 41.29	9235 ± 41.21	
	Roots	16987 ± 10.24	12347 ± 30.24	10276 ± 17.89	11325± 23.54
Copper	Sheet	412 ± 14.38	1023 ± 31.45	987 ± 29.84	
mg/kg	Stems	568 ± 56.21	1124 ± 12.78	896 ± 21.45	
	Roots	667 ± 22.25	1542 ± 14.78	972 ± 36.45	8954 ± 46.32
Zinc	Sheet	8654 ± 16.99	10235 ± 35.64	8794 ± 12.48	
mg/kg	Stems	8890 ± 17.84	10894 ± 45.69	9321 ± 45.32	
	Roots	9321 ± 22.14	12365 ± 35.45	10234 ± 13.4	9651 ± 41.78
Gold	Sheet	<ld< th=""><th><ld< th=""><th><ld< th=""><th></th></ld<></th></ld<></th></ld<>	<ld< th=""><th><ld< th=""><th></th></ld<></th></ld<>	<ld< th=""><th></th></ld<>	
µg/kg	Stems	<ld< td=""><td><ld< td=""><td><ld< td=""><td></td></ld<></td></ld<></td></ld<>	<ld< td=""><td><ld< td=""><td></td></ld<></td></ld<>	<ld< td=""><td></td></ld<>	
	Roots	5.7 ± 0.2	<ld< td=""><td><ld< td=""><td><ld< td=""></ld<></td></ld<></td></ld<>	<ld< td=""><td><ld< td=""></ld<></td></ld<>	<ld< td=""></ld<>

Table2: Variation in the concentration (mean \pm SD) of elements in the analyzed samples from Andrafialava.

LD : Detection limit.

Average sample concentration from Ankaramy

In summary, we reveals variations in the concentrations of iron, copper, zinc, and gold among the analyzed plant species from Ankaramy. The concentrations of these elements differ across different plant parts, emphasizing the importance of considering specific plant tissues when studying elemental composition. The findings also suggest potential differences in the accumulation and distribution of elements among plant species, which can be influenced by various environmental and biological factors.

Table3: Change in the concentration (mean ± SD) of elements in the analyzed samples from Ankaramy.

Element	Parts analysed	Albizia lebbeck	Flacourtia Ramontchi	Annona senegalensis	Imperata cylindrica
Tron	Sheet	5456 ± 24.56	3625 ± 13.25	6669 ± 75.21	
Iron	Stems	6321 ± 27.74	4178 ± 18.98	7012 ± 47.78	
mg/kg	Roots	6914 ± 10.24	5021 ± 21.34	10230 ± 33.54	3654 ± 32.54
Connor	Sheet	1214 ± 22.22	1012 ± 36.45	3201 ± 12.02	
Copper mg/kg	Stems	6668 ± 19.87	1098 ± 31.01	3321 ± 39.97	
ilig/kg	Roots	7324 ± 43.21	2032 ± 36.69	4032 ± 44.5	5487 ± 26.69
Zinc	Sheet	9874 ± 12.47	2034 ± 14.45	12547 ± 6.32	
mg/kg	Stems	9997 ± 30.12	8659 ± 23.54	12555 ± 32.54	
	Roots	11475 ± 32.21	9321± 23.02	13256 ± 22.1	999 ± 12.04
Gold	Sheet	<ld< th=""><th><ld< th=""><th><ld< th=""><th></th></ld<></th></ld<></th></ld<>	<ld< th=""><th><ld< th=""><th></th></ld<></th></ld<>	<ld< th=""><th></th></ld<>	
	Stems	<ld< td=""><td><ld< td=""><td><ld< td=""><td></td></ld<></td></ld<></td></ld<>	<ld< td=""><td><ld< td=""><td></td></ld<></td></ld<>	<ld< td=""><td></td></ld<>	
µg/kg	Roots	<ld< td=""><td>8.8 ± 0.15</td><td>7.5 ± 0.3</td><td><ld< td=""></ld<></td></ld<>	8.8 ± 0.15	7.5 ± 0.3	<ld< td=""></ld<>

LD : Detection limit.

Average sample concentration from Ambilo

In general, the data illustrates differences in the levels of iron, copper, zinc, and gold in the plant species analyzed from Ambilo. There are variations in the concentrations of these elements across different parts of the plants, suggesting diverse patterns of accumulation and distribution. The results emphasize the capacity of specific plant species, such as Imperata cylindrica and Albizia lebbeck, to accumulate elevated levels of certain elements, whereas others like Flacourtia Ramontchi demonstrate lower concentrations. These variances can be attributed to a range of environmental factors and the physiological characteristics of the plants.



Table 4: Variation in the concentration (mean ± SD) of elements in the analyzed samples from Ambile							
Element	Parts	Albizia	Flacourtia	Annona	Imperata		
	analysed	lebbeck	Ramontchi	senegalensis	cylindrica		
Tron	Sheet	12457 ± 21.5	1975± 20.21	3215 ± 17.36			
Iron	Stems	18235 ± 22.1	3254 ± 30.41	4687 ± 12.45			
mg/kg	Roots	21776 ± 29.97	6654 ± 20.23	6354 ± 9.65	8974 ± 31.04		
Common	Sheet	891 ± 78.74	354± 55.3	998 ± 18.36			
Copper	Stems	958± 32.6	784 ± 21.4	1023 ± 12.47			
mg/kg	Roots	1032 ± 98.32	875 ± 30.14	1047 ± 22.5	10254 ± 25.31		
Zinc	Sheet	10501 ± 22.14	3215 ± 32.54	9032 ± 20.12			
	Stems	10774 ± 66.45	4587 ± 14.08	10325 ± 13.33			
mg/kg	Roots	10954 ± 66.2	5001 ± 22.5	10897 ± 19.6	11568 ± 16.66		
Cold	Sheet	<ld< th=""><th><ld< th=""><th><ld< th=""><th></th></ld<></th></ld<></th></ld<>	<ld< th=""><th><ld< th=""><th></th></ld<></th></ld<>	<ld< th=""><th></th></ld<>			
Gold µg/kg	Stems	<ld< td=""><td><ld< td=""><td><ld< td=""><td></td></ld<></td></ld<></td></ld<>	<ld< td=""><td><ld< td=""><td></td></ld<></td></ld<>	<ld< td=""><td></td></ld<>			
μą/ kg	Roots	7.4 ± 0.1	<ld< td=""><td>8.8 ± 0.2</td><td><ld< td=""></ld<></td></ld<>	8.8 ± 0.2	<ld< td=""></ld<>		

LD : Detection limit

4. DISCUSSION

The X-ray fluorescence (XRF) technique plays a significant role in the analysis of total elements in different environmental samples and various types of industrial products. It has been widely used for metal determination in soils, and the portable XRF is among the techniques recommended by the United States Environmental Protection Agency [8]. Additionally, XRF has been employed for analyzing minor elements in cement products in Iraq [9]. It is also utilized in determining the origin and authenticity of precious stones such as beryl, ruby, sapphire, and emerald. The presence of specific elements influences the color and properties of these gemstones. For instance, chromium (Cr), iron (Fe), and titanium (Ti) contribute to the color of rubies and sapphires, while chromium (Cr) and vanadium (V) primarily affect the color of emerald or beryl. Furthermore, impurities in precious stones can help identify their origin. Therefore, the identification of gallium (Ga), vanadium (V), and zirconium (Zr) in rubies and sapphires is crucial for confirming their authenticity as natural stones. Similarly, the presence of gallium (Ga), scandium (Sc), rubidium (Rb), and cesium (Cs) in emerald and beryl indicates their genuine nature. Conversely, the presence of platinum (Pt) in emerald or beryl indicates that the stones are synthetic.

Regarding the Mantaly Maro case, the analysis results reveal that the samples from Mantaly Maro of the four plants exhibit lower average concentrations of iron, copper, and zinc. Additionally, trace amounts of gold were detected in the root part of the *Albizia lebbeck* plant with an average content of $5.3 \pm 0.5 \ \mu g.kg^{-1}$. Similarly, the plant *Annona senegalensis* exhibited a gold concentration of $7.8 \pm 0.4 \ \mu g.kg^{-1}$. On the other hand, *Flacourtia Ramontchi* and *Imperata cylindrica* did not show detectable concentrations of gold in the tested parts.

In the Andrafialava case, the analysis results indicate that the samples from Andrafialava of the four plants display lower average concentrations of iron, copper, and zinc. Additionally, trace amounts of gold were found in the root part of the *Albizia lebbeck* plant with an average content of $5.7 \pm 0.2 \ \mu g.kg^{-1}$. However, the concentrations of gold in *Flacourtia Ramontchi,* Annona senegalensis, and *Imperata cylindrica* were below the detection limit in the tested parts.

Concerning the Ankaramy case, the analysis results demonstrate that the samples from Ankaramy of the four plants exhibit lower average concentrations of iron, copper, and zinc. Trace amounts of gold were detected in the root part of the Flacourtia Ramontchi plant with an average content of $8.8 \pm 0.15 \ \mu g.kg^{-1}$. Similarly, the plant Annona senegalensis showed a gold concentration of $7.5 \pm 0.3 \ \mu g.kg^{-1}$. However, the concentrations of gold in *Albizia lebbeck* and *Imperata cylindrica* were below the detection limit in the tested parts.

The results of analyses show that the samples coming from Ambilo from the four plants contain iron, copper, zinc with an average lower concentration. We also found the trace of gold on the Plant *Albizia lebbeckwith* a very low content on average of $7.4 \pm 0.1 \,\mu$ g.kg⁻¹ in the root part, likewise on the plant Annona senegalensis a concentration of $8.8 \pm 0.2 \,\mu$ g.kg⁻¹.The concentration is below the detection limit on *Flacourtia Ramontchi* and *Imperata cylindrica* on the test parts.

5. CONCLUSION

The method of X-ray fluorescence analysis was used to determine the chemical elements present in these plants. The analysis results revealed the presence of four sought-after chemical elements, namely iron, copper, zinc, and gold, in all the examined samples. Trace amounts of gold were detected in the roots of the *Albizia lebbeck, Flacourtia Ramontchi*, and *Annona senegalensis* plants, indicating its occurrence at very low levels. The presence of such trace amounts of gold in the roots suggests the potential for gold prospecting in the rural commune of Betsiaka. However, further investigations and comprehensive studies are necessary to accurately assess the extent and viability of gold deposits in this area.

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