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**SHORT COMMUNICATION**

# DETERMINATION OF THE MINOR AND TRACE ELEMENTS IN BIRINIWA'S TIN PYRITE AND ORNAMENTAL LEAD/ZINC ORE USING NEUTRON ACTIVATION ANALYSIS

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**ABSTRACT.** Preliminary results of analysis of two common decorative/ornamental minerals analysed for minor and trace elements with the neutron activation analysis technique are discussed. The samples of interest were the Biriniwa tin pyrite, which the local indigenous used to paint their huts and the ornamental lead which women use to adorn their eyelashes nation-wide. These samples were irradiated along the certified reference sample, CANMET-BLI, with thermal neutron at the Julich Reactor Centre, Julich, Germany. The prominent elements determined in the ornamental lead included zinc (35.8%), iron (6.15%), Na, Sb, Cd, Hg, Ag and Co at trace level (μg $g^{-1}$). Tin pyrite sample was found to contain traces of Na, K, As, Br, Sb, Fe, La, Nd, Sm and Ce as the prominent impurities. Lead and tin, the major elements, respectively, of the lead/zinc ore and tin pyrite samples were determined by classical methods.

**KEY WORDS:** Ornamental minerals, Tin pyrite, Ornamental lead, Neutron activation analysis

## INTRODUCTION

The quest for beauty of persons, object and environment has been on with humanity since the beginning of human civilization. In the Bible, Moses ordered the decoration of the sanctuary objects of worship and altar with gold, silver and bronze [1, 2]. During the Jewish war (A. D. 66-73) the molten gold used to beautify the Jerusalem's Temple partly encouraged the conquering Roman soldiers to pillage and loot the temple [1-4]. Humanity has used paints, metals, dyes, minerals and gemstones to beautify their bodies, houses, temples and environment [1-6]. Tin is a metal used in the manufacture of containers, artefacts and other objects. Tin mines occur principally in Britain, Malaysia and Nigeria [6-9]. The exploitation of the Nigerian tin mines in Jos Plateau area has been going since the colonial era. The tin ores from the Plateau is mainly cassiterite. Recent findings by the Nigerian Geological Surveys in Kaduna, Nigeria reported the presence of tin ores in Biriniwa area of Jigawa State of Nigeria in form of pyrites. However, no appreciable exploitation of this mineral is going on. Locally, the Biriniwa indigenous use the mineral to whitewash their houses. In Hausa language, this mineral is called *Maramara*. However, to encourage some meaningful exploitations of this mineral, the need to analyse the ore chemically arose, hence, this is the focus of this report.

In Africa, particularly in Nigeria, prior to the advent of modem cosmetics, womenfolk had developed local cosmetics. Cosmetics like red stone, titanium oxide, vegetable dyes and ornamental lead in form of pencil has been in use. Mineral ore in form of shining ornamental lead has been fashioned into lead pencil and used to darken eyelashes and brows. This mineral is commonly sold in markets all over the nation. However, no work has been published which

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examines implication to health of this mineral. We hope to make a first contribution, which gives an indication of the concentration levels of toxic elements that citizens may be exposed to.

In order to accomplish this, a sensitive, multi-element analytical technique is essential to obtain the much-needed chemical information on these minerals. Neutron activation analysis is a method of choice [10-17]. This technique has been employed in analysis of food, mineral, clinical, and environmental sample [10-17]. Recently, Oladipo *et al.* [10] reported the trace element profile of some shaving powder samples commonly marketed in Nigeria. In this analysis, the two mineral samples along with a certified reference sample, CANMET-BU, were subjected to neutron activation analysis. The two real samples were also analysed employing classical methods in order to determine their respective major elements on interest that were hitherto not accounted for in neutron activation analysis.

## EXPERIMENTAL

*Samples and sample preparation*. The sample of tin ore was obtained from Biriniwa in Jigawa State of Nigeria where this mineral occurs. The ornamental lead was purchased at Sabongari market in Zaria, Kaduna State, Nigeria. The two samples were milled to powder, dried and stored in plastic containers.

*Neutron activation analysis*. The samples (real and reference) were separately weighed (1.0 g. each) into NAA ampoule. The samples were irradiated and analysed at Julich Reactor Centre, Julich, Germany. The samples were irradiated with a neutron flux of 3.2 x $10^{12}$ n $cm^{-1}$ $s^{-1}$ for about ten minutes, cooled for a day before counting using Ge(Li) detector. The $\gamma$-ray spectra were resolved with data resolving software of the dedicated computer attached to the detector and used to calculate the concentration of the resolved nuclides.

*Classical analysis of the samples*. The lead content of the ornamental lead as well as the tin content of tin pyrite sample were determined gravimetrically using their respective procedures as outlined by Vogel [18]. 1.0 g of tin pyrite was dissolved in 10 $cm^3$ of 1.0 M HCl, the dissolution was aided with heating. The residue was filtered and collected on an ashless filter paper for the determination of acid-insoluble ash content after ignition at 850-900 °C. The filtrate was diluted to 100-$cm^3$ mark with distilled water. 1.0 g each of lead/zinc ore was dissolved in 10 $cm^3$ of concentrated nitric acid, the residue was similarly used for acid-insoluble ash content determination.

## RESULTS AND DISCUSSION

The results of the various analyses carried out are as reported in Tables 1-3. The results of the analysis of the certified reference sample, CANMET-BLI, are shown on Table 1, while Table 2 depicts the results of the analysis of the real samples, tin and ornamental lead. Both analyses were accomplished with neutron activation analysis technique. Table 3 contains the results obtained from the classical analysis of both ores.

In Table 1, four elements; Fe, K, Na and U were determined with appreciable accuracy as the concentration determined for each element approached the corresponding certified value obtained as the reference. In most cases the NAA concentration of each element was close to the range of values indicated in the reference. This shows that this technique could be relied upon for relatively accurate, reproducible and precise analysis of samples with complex matrix.

Table 1. Analysis of CAN-MET BLI using neutron activation analysis (NAA).

| Element | NAA concentration | Certified value |
|---|---|---|
| Fe (%) | 5.08±0.1 | 4.57-4.96 |
| K (%) | 1.17±0.01 | 0.99-1.09 |
| N a (%) | 3.82±0.01 | 3.85-3.88 |
| U | 260 | 220 -265 |

Concentration in μg $g^{-1}$ (ppm) except otherwise stated.

Table 2. Neutron activation analysis of tin pyrite and ornamental lead.

| Element | Tin pyrite | Ornamental lead |
|---|---|---|
| Na | 890 | 123 |
| K | 4900 | <2000 |
| Ga | 15.0 | 85 |
| As | 0.92 | 2.0 |
| Br | 2.2 | <1.0 |
| Sb | 0.89 | 88.0 |
| La | 36.0 | 0.44 |
| Sm | 7.5 | <0.1 |
| Eu | 1.6 | <0.2 |
| W | <1.0 | 4.0 |
| Sr | 1.6 | <0.2 |
| Fe | 5580 | 6.15% |
| Co | 5.3 | 119 |
| Zn | <20.0 | 35.8% |
| Se | <4.0 | 9.0 |
| Ag | <2.0 | 88.0 |
| Cd | <6.0 | 878.0 |
| Cs | 0.96 | 2.0 |
| Ce | 87.0 | <5.0 |
| Nd | 47.0 | 30.0 |
| Tb | 1.7 | <0.5 |
| Yb | 5.2 | <0.4 |
| Hf | 4.7 | <1.0 |
| Ta | <0.4 | <0.4 |
| Ir | <0.02 | <0.02 |
| Au | <0.02 | <0.02 |
| Hg | <2.0 | 49.0 |
| Th | 5.3 | <0.2 |
| U | 4.1 | <0.5 |

Concentration in μg $g^{-1}$ (ppm) except otherwise stated.

The results in Table 2 show the concentration of the various common elements determined in both samples. In both samples, a total of thirty elements were detected in appreciably measurable concentrations. In the Biriniwa's tin ore, Na, K, As, Br, Sb, La, Sm, Eu, Sc, Cr, Fe, Co, Ce, Cs, Nd, Th, Hf, Th and U were detected in measurable quantities at μg $g^{-1}$ level. Other elements such as Ga, W, Zn, Se, Ag, Cd, Ta, Ir, Au and Hg occurred below their respective detection limits. However, all these elements determined were in trace quantities (μg $g^{-1}$). In other words all these elements could be regarded as impurities in this sample [12-14]. The ornamental lead characteristically contained zinc as one of its major element amounting to 35.8% (w/w) of the sample along with 6.15% of iron. The other elements detected in measurable quantities included Na, Ga, As, Sb, La, Co, Ag, Cd, Cs and Hg. Elements like Sb, Ag, Cd and Hg normally co-exist with lead, zinc and gold ore [12-14]. Other elements like K, Br, Sm, Eu, W, Sc, Cr, Se, Ce, Nd, Th, Yb, Hf, Ir, Au, Th and U were found to occur below detection limit for the calibration of these elements. In the two samples the respective major elements of interest could not be determined probably due to the instrument's calibration.

The results in Table 3 are based on the classical analysis of the two samples. Acid insoluble ash content of 32.33% was recorded for the pyrite due to the silica content. The tin content was about 63.96% for this mineral. The ore was physically different from the casssiterite currently exploited in Nigeria. The ornamental lead contained about 39.32% Pb relative to 35.8% Zn. This result shows that both ores were rich in their respective metals.

Table 3. Results of the classical analysis of the ores.

| Parameter | Tin pyrite | Lead/zinc ore |
|---|---|---|
| Acid insoluble ash | 32.33% | |
| Sn | 63.96% | n.d. |
| Pb | n.d. | 39.32% |

n.d. = not detectable.

The use of ornamental lead as cosmetic may not bode well for the health of the users and their offspring since the accumulation of the particularly toxic elements in their systems build upon prolong application. In a situation where a lady applies 10.00 g topically on her brow and lashes annually, she may accumulate 0.85 mg Ga, 0.2 mg As, 0.88 mg Sb, 40 μg W and 1.19 mg Co. In addition, 615 mg Fe, 3.6 g Zn, 880 μg Ag, 8.78 mg Cd, 3.95 g Pb and 490 μg Hg may also be absorbed annually. The build up of this over the year may not bode well for the user. Therefore the need to discourage the use of this cosmetic becomes paramount, as the elemental content is a source of potential health and possibly genetic hazard in case of the offspring.

## CONCLUSION

The minor and trace element content of Biriniwa's tin ore as well as those of the ornamental lead/zinc were determined employing the neutron activation analysis technique. In addition, the major elements hitherto not accounted for in neutron activation analysis were determined by classical methods. The results were discussed both on the elemental content ground as well as the health implication of the heavy metals common with them. The use of the ornamental lead ore as cosmetics needs to be discouraged as it can introduce heavy metal poisoning to the users blood system as well as their offspring. These minerals are mined locally, but not yet effectively exploited. Further work to sample a larger selection of the ore body needs to be done in order to ascertain whether the nation can reap the economic benefit from the exploitation of the ores.

## REFERENCES

1. *The Holy Bible*, Today English Version, American Bible Society: New York; **1976**.
2. Josephus, F. *The Jewish War*, Penguin Publishers: New York; **1976**.
3. Michener, J.A. *The Source*, Corgi Publisher: New York; **1978**.
4. *Kirk Orthner Encyclopaedia of Chemical Technology*, 4th ed., Vol. 2, John Wiley: New York: **1992**; pp 330–342.
5. Read, H.H. *Rutley's Elements of Mineralogy*, Thomas Murby and Company: London; **1960**.
6. Nigerian Geological Surveys, Kaduna, Nigeria, **1989**; *Personal communication.*

7. *Geological Map of Nigeria*, Geological Surveys Department, Kaduna, Nigeria.
8. Austen, G.T. *Shreve's Chemical Process Industry*, 4th ed., McGraw-Hill: London; **1984**.
9. Lee, J.D. *A New Concise Inorganic Chemistry*, 3rd ed., Nostrand Reinhold Company Limited: London; **1981**.
10. Oladipo, M.O.A.; Lori, J.A.; Bonire, J.J.; Ajayi, O.O. *J. Radioanal. Nucl. Chem., Articles* **1997**, 224, 167.
11. Ewa, I.O.B.; Elegba, S.B.; Adetunji, J. *J. Radioanal. Nucl. Chem., Letters* **1996**, 231, 213.
12. Oladipo, M.O.A.; Rehman, F. *Spectroscopy Letters* **1991**, 24, 577.
13. Oladipo, O.A.; Adeleye, S.A.; Elegba, S.B. *J. Radioanal. Nucl. Chem., Articles* **1989**, 134, 277.
14. Jacobs, F.S.; Filby, R.H. *Anal. Chem.* **1983**, 55, 74.
15. Alfassi, Z.B. *Anal. Chem.* **1983**, 55, 796.
16. Morthy, R.S.; Ryan, D.E. *Anal. Chem.* **1983**, 55, 681.
17. Opelanio, L.R.; Rack, E.P. *Anal. Chem.* **1983**, 55, 671.
18. Vogel, A.I. *A Textbook of Quantitative Inorganic Analysis including Elementary Instrumental Analysis*. 3rd ed., Longman-Green Company limited: London; **1979**.