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MULTIELEMENT ANALYSIS OF NIGERIAN CHEWING STICKS BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

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In Nigeria, various parts of various species of native plants have long been used for dental hygiene, with reportedly considerable effectiveness. These materials are known as "chewing sticks". This study was an effort to ascertain whether any unusual trace element concentrations might be present in Nigerian chewing sticks. Results are presented for 17 elements (Na, Mg, Al, Cl, K, Ca, Sc, V, Mn, Fe, Co, Zn, Br, Cs, La, Sm, Au) detected and measured in 12 species of such plants, via instrumental thermal-neutron activation analysis.

Introduction

In Nigeria, the traditional method of dental hygiene involves brushing the teeth with some special types of wooden plant species, locally known as "chewing sticks". Even with the influence of Western culture, this age-old tradition remains. In addition, different parts of these same plants are also employed in various forms for medicinal purposes. In recent years, there has been a growing interest in investigating the chemical and pharmacological properties of local herbs and drugs in Nigeria.[1–4] In the present study, the method of reactor-flux instrumental (thermal) neutron activation analysis (INAA) was employed to analyze samples of twelve different species of chewing sticks for their detectable major, minor, and trace elements. The twelve species of plants analyzed are listed and briefly described in Table 1.

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Table 1
Nigerian chewing stick plants* analyzed by INAA

Common name	Scientific name	Brief description	Parts used for chewing sticks
1. Orin Ata	Fagara Leprieurii	Tall tree	Roots
2. Orogbo	Garcinia Kola	Tall tree	Trunk or roots
3. Meyinro (or Meyinfun)	Scrindeia Warneckei	Shrub	Stem
4. Pako Dudu (or Pako Ayin)	Anogeissus Leiocarpus	Tall tree	Roots
5. Pako Ijebu (or Ewurodo)	Massularia Accuminata	Small tree	Trunk
6. Ewuro	Vernonia Amygdalina	Small tree	Roots
7. Idi Pupa	Terminalia Glaucescens	Tall tree	Roots
8. Idi Funfun	Terminalia Laxiflora	Tall tree	Roots
9. Igi Emi (or Igi Ori)	Bytyrospernum Paradoxum	Medium tree	Roots
10. Egbo Egbesi	Nauclea Latifolia	Small tree	Roots
11. Orin Odan**	Vitex Doniana	Tall tree	Trunk
12. Pako Calabar	(no information available)		

*Courtesy of the Museum of Natural History, University of Ife, Ile-Ife, Nigeria.
**Courtesy of the Forestry Research Institute of Nigeria, Ibadan, Nigeria.

Experimental

As an advance rough guide to the best irradiation and decay times to use (to detect the largest number of elements in only a few irradiations and counts of each sample), and to the maximum sample sizes to use under these various conditions (in order to keep the analyzer deadtime at only about 2%), the INAA Advance Prediction Computer Program (APCP)[5] was used. As input to the APCP, a typical woody-plant composition was used: the mean elemental composition of Angiosperms, taken from BOWEN.[6] The BOWEN compilation provided mean values for 21 elements (Ag, Al, Ca, Cd, Co, Cr, Cu, Fe, Ga, K, Mg, Mn, Mo, Na, Ni, Pb, S, Sn, U, V, Zn). For the conditions specified (Φ of 10^{12} n $\cdot$ cm$^{-2} \cdot$ s^{-1}, counting 2 cm from a 90 cm^3 ("15%") coaxial Ge(Li) detector and 4096-channel pulse-height analyzer, maximum counting rate at SOC of 1000 cps or a lg maxi-

mum sample weight), the APCP predicted that 12 of these 21 input elements should be detectable to a relative photopeak measurement precision of ±50% or better, if all the regular 12 stepped sets of t_i, t_d, t_c conditions were employed: Al, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, V, Zn.

Using the above APCP output, using some interpolations and practical restrictions, it was decided that 11 of the 12 elements (all except Cr) should be detectable under the four measurement conditions selected:

(1) $\Phi = 2.5 \cdot 10^{10}$, $t_i = 3$ min, $t_d = 1.5$ min, $t_c = 3$ min, 0.3 g sample.
(2) $\Phi = 1 \cdot 10^{12}$, $t_i = 60$ min, $t_d = 3$ days, $t_c = 17$ min, 0.3 g sample.
(3) $\Phi = 1 \cdot 10^{12}$, $t_i = 120$ min, $t_d = 2$ weeks, $t_c = 17$ min, 1 g sample.
(4) $\Phi = 1 \cdot 10^{12}$, $t_i = 120$ min, $t_d = 5$ weeks, $t_c = 17$ min, 1 g sample.

All the sample weights are for dried wood, and each sample was accurately weighed. These four measurement conditions were then also checked by the APCP. They were selected not only to allow measurement of the 11 indicated elements, but also other elements possibly present, but not members of the 21-element Angiosperm input, including elements whose (n, γ) products were short-lived, medium-lived, or long-lived.

The APCP was extremely useful in this study, in that it: (1) predicted correctly the 11 elements (out of the 21 Angiosperm input elements) that should be measurable, (2) predicted correctly that the other 10 of the 21 input elements would not be measurable, and (3) predicted correctly that the sample weights chosen would not result in excessive analyzer deadtimes. In addition to the 7 predicted elements (Au, Br, Cl, Cs, La, Sc, Sm) not included in the 21 Angiosperm input elements were also detected and measured. The ppm values obtained for 17 of the elements detected in these twelve plant samples (all except Cu) are presented in Table 2. Copper was also detectable, but only by means of the 511 keV β^+ annihilation peak of 12.8 hour ^{64}Cu. This peak included a large contribution from 511 keV photons generated in the detector shield by pair-production interaction in it by the high-energy gamma rays of ^{24}Na. At the time of these measurements, no quantitative correction for the ^{24}Na contribution was available, so no copper results were obtained.

During the analyses of the samples, suitable standard solutions (of the same volume as the samples) of the 11 expected elements were activated and counted under the same conditions as the samples. Subsequently, standards of the 7 unanticipated elements detected in the samples were also prepared and activated and counted similarly. Preparation of the standards was also greatly expedited by use of the APCP, giving the number of micrograms of each element needed, for each

Table 2
Measured element concentrations (ppm, by INAA) of 17 elements in 12 different kinds of Nigerian chewing sticks

Common name	Al K Fe	V Na Sc	Ca Br Zn	Mg La Cs	Cl Sm Co	Mn Au
1. Orin Ata	9,100±370 3,400±60 75±42	0.25±0.12 98±1 0.12±0.03	10,000±1,900 7,2±0.2 155±28	1,600±250 14.6±0.4 0.41±0.06	937±69 0.52±0.01 0.21±0.08	15±2 1.18±0.04
2. Orogbo	28,700±1,200 3,350±67 1,100±110	2.30±0.40 32±1 0.63±0.06	9,000±2,000 2.4±0.1 213±37	850±610 4.40±0.18 0.73±0.09	124±79 0.27±0.01 0.88±0.14	71±6 1.25±0.04
3. Meyinro (or Meyinfun)	1,300±72 9,030±110 71±26	0.13±0.08 38±1 ⩽0.09	26,400±4,700 2.6±0.1 184±25	280±230 0.36±0.10 0.20±0.05	824±85 0.034±0.005 0.15±0.05	14±3 1.02±0.04
4. Paku Dudu (or Pako Ayin)	264±25 5,440±79 45±25	⩽0.09 50±1 ⩽0.03	36,000±6,200 4.8±0.2 145±22	840±200 2.30±0.13 0.05±0.03	222±49 0.120±0.006 0.28±0.06	6±2 1.03±0.03
5. Pako Ijebu (or Ewurodo)	204±21 1,590±40 42±20	⩽0.10 28±1 ⩽0.04	1,900±620 0.8±0.1 153±21	972±196 0.08±0.05 0.07±0.03	135±41 ⩽0.006 0.13±0.05	58±5 0.92±0.03
6. Ewuro	211±23 8,500±120 54±31	⩽0.12 24±1 ⩽0.03	1,100±450 4.8±0.2 135±31	340±210 3.00±0.16 ⩽0.04	1,360±130 0.064±0.006 0.12±0.08	17±4 1.42±0.05

7. Idi Pupa	2,050±100	0.26±0.14	22,900±4,200	1,480±350	654±93	15±3
	3,540±73	93±1	4.4±0.2	1.50±0.14	0.060±0.006	1.26±0.05
	181±45	⩽0.10	179±29	⩽0.08	0.31±0.08	
8. Idi Funfun	2,750±150	0.18±0.13	25,400±5,000	470±200	187±76	12±4
	4,890±110	49±1	3.9±0.2	4.8±0.2	0.19±0.01	2.05±0.09
	196±68	0.07±0.05	379±53	⩽0.16	0.46±0.14	
9. Igi Emi	534±23	⩽0.09	5,380±1,100	1,950±260	1,050±86	9±2
(or Igi Ori)	13,500±130	29±1	3.1±0.1	5.1±0.2	0.110±0.006	0.77±0.03
	⩽37	⩽0.03	118±18	0.010±0.005	0.10±0.04	
10. Egbo Egbesi	5,050±230	0.57±0.20	9,050±2,100	4,560±650	255±89	34±6
	9,380±160	52±1	3.5±0.2	4.3±0.2	0.21±0.01	2.00±0.06
	453±105	⩽0.11	195±47	0.11±0.08	0.68±0.15	
11. Orin Odan	2,020±110	0.16±0.09	33,700±6,000	930±250	⩽49	24±3
	4,110±76	49±1	4.8±0.2	3.40±0.15	0.130±0.006	1.04±0.03
	60±37	⩽0.05	118±22	⩽0.04	0.30±0.07	
12. Pako Calabar	198±21	⩽0.11	1,200±480	⩽190	63±25	67±6
	1,280±46	24±1	0.9±0.1	⩽0.11	⩽0.005	1.19±0.04
	⩽29	0.06±0.02	120±25	0.17±0.05	0.10±0.05	

Note: The ± figure shown after each value represents the uncertainty of the value, expressed as one standard deviation—calculated only from the counting statistics. Values shown as ⩽ mean that no peak was detectable and the value shown is a one sigma upper limit, calculated from the counting statistics.

Table 3
(n, γ) Radionuclides and
gamma-ray peaks measured

(n, γ) radionuclide	Half-life	keV of γ-ray peak(s)
^{28}Al	2.31 m	1779
^{52}V	3.76 m	1434
^{49}Ca	8.8 m	3083
^{27}Mg	9.45 m	1014
^{38}Cl	37.3 m	1642
^{56}Mn	2.58 h	1811
^{42}K	12.5 h	1525
^{24}Na	15.0 h	1368, 2754
^{82}Br	35.9 h	554
^{140}La	40.3 h	487, 1595
^{153}Sm	47.1 h	103
^{198}Au	2.70 d	412
^{59}Fe	45.6 d	1099
^{46}Sc	83.9 d	889
^{65}Zn	245 d	1115
^{134}Cs	2.07 y	605
^{60}Co	5.24 y	1332

irradiation and decay condition, so that its total counting rate at SOC would be about 1000 cps. All samples and standards were contained in sealed polyethylene vials during reactor irradiation, and then transferred to fresh vials for counting. The 3 minute irradiations at $2.5 \cdot 10^{10}$ n · cm^{-2} · s^{-1} thermal-neutron flux were made sequentially in the regular pneumatic-tube position of the reactor (3 second transit time), operating the reactor at only 1% of full power. The 1-hour and 2 hour irradiations at $1 \cdot 10^{12}$ n · cm^{-2} · s^{-1} flux were made in the 40-tube rotary specimen rack of the reactor, operating the reactor at full 250 kw power; in these longer irradiations, all the samples and standards were activated simultaneously.

The radionuclides, their halflives, and their gamma-ray peaks measured, for the various (n, γ) products, are given in Table 3. Due to the overlap of the 844 keV γ-ray peak of ^{27}Mg with the 847 keV peak of ^{56}Mn, their smaller but uncomplicated peaks were used for measurement: the 1014 keV peak of ^{27}Mg, and the 1811 keV peak of ^{56}Mn. Overlap of the 1115 keV peak of ^{65}Zn with the 1120 keV peak of ^{46}Sc was resolved by use of the ^{46}Sc 1120/889 keV peak ratio of the Sc standard and the 889 keV ^{46}Sc peak of the sample.

Results and discussion

Comparison of the mean experimental values of the twelve species of chewing stick plants with the mean Angiosperm values, for the ten elements, Al, Ca, Co, Fe, K, Mg, Mn, Na, V, and Zn, reveals that 5 of the elements (Co, Fe, K, Mg, Zn) show mean experimental values that are within a factor 3, one way or the other, of the corresponding mean Angiosperm value. However, the chewing stick plant mean values for Al and Ca are about 8 times larger than the Angiosperm mean values, whereas their mean values for Mn and Na are about 25 times smaller than the Angiosperm mean values, and their mean value for V is about 4.5 times smaller than the Angiosperm mean value.

The above comparison of mean values with the mean Angiosperm values is of interest, but attention must also be directed to the wide range of values found for some elements amongst the 12 different species of chewing stick plants. For example, for one element (Al) the maximum value found is 145 times as large as the minimum value found. For 4 elements (Ca, Fe, Mg, V), the maximum/minimum ratio is in the range of 24–38/1. For the other 5 elements (Co, K, Mn, Na, Zn), the maximum/minimum ratio is smaller, ranging from 3–12/1. The corresponding ratios for the 7 unanticipated elements are 3/1 for Au, 9/1 for Br, 28/1 for Cl, 73/1 for Cs, 180/1 for La, 21/1 for Sc, and 100/1 for Sm.

For 7 elements (Al, Ca, Co, Fe, Mg, V, and Zn), the mean Angiosperm value falls within the range of the 12 sample values for the particular element. The mean K value for angiosperms (14 000 ppm) is slightly larger than even the largest of the K values for the 12 chewing stick wood samples. For Mn, the mean Angiosperm value is 8.9 times larger than even the largest chewing stick Mn value. For Na, the mean Angiosperm value is 12 times larger than even the largest chewing stick Na value.

Whether or not the elemental compositions of these various Nigerian chewing stick plants are in any way related to the fact that rural Nigerians (who use chewing sticks extensively for dental hygiene) have a relatively low incidence of dental caries is of course not known. In this connection, the determination of fluorine in the samples would be of particular interest, but this does not appear to be feasible by INAA even if irradiation, decay, and counting times appropriate to the half-life of fluorine-20 (11.2 seconds) were employed. However, this first study of the major, minor, and trace elements detectable in Nigerian chewing stick woods by INAA may provide useful information for other studies of dental caries, or for other types of studies.

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References

1. L. OGUNKOYA, O. O. OLUBAJO, D. S. SONDHA, Phytochemistry, 11 (1972) 2361.
2. L. OGUNKOYA, O. O. OLUBAJO, D. S. SONDHA, Phytochemistry, 11 (1972) 3093.
3. F. EL-SAID, S. O. FADULU, J. O. KUYE, E. A. SOFOWORA, Lloydia, 34 (1971) 172.
4. S. O. FADULU, Planta Medica, 27 (1975) 122.
5. V. P. GUINN, E. GARZANOV, E. CORTES, J. Radioanal. Chem., 43 (1978) 599.
6. H. J. M. BOWEN, Trace Elements in Biochemistry, Acad. Press, New York (1966) Ch. 5.