

Analysis of Various Nigerian Foodstuffs for Crude Protein and Mineral Contents by Neutron Activation

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ABSTRACT

Various Nigerian foodstuffs were analysed for crude protein and some important nutrient minerals, Ca, Fe, K and P, using the neutron activation technique. The protein content of the staple foods, cassava and its products, cocoyam, yam, rice and plantains, varies from about 1% to 12.8%, while the grains, maize, guinea corn and millet, as well as African breadfruit seeds and some popular vegetables, have a relatively high protein content. Corrections for the relevant reaction interferences in nitrogen determination were carried out. The precision of the sample analyses varied in the range ± 2.1 to $\pm 6.3\%$.

INTRODUCTION

Recently, the method of fast neutron activation analysis (FNAA) has been specifically applied to the determination of nitrogen in various organic and inorganic materials such as foodstuffs (Brune & Arrayo, 1971; Rao *et al.*, 1972; Chuang *et al.*, 1977; Ndiokwere, 1982), animal feeds (Bibby & Champion, 1974), fertilizer and plant materials (Srapenyants & Savelier, 1977; Ndiokwere & Jerabek, 1983). This technique, unlike the traditional, chemical Kjeldahl method, is not hampered by the various forms of nitrogen in samples, even in complex matrices.

The FNAA method is based on the nuclear reaction, $^{14}\text{N}(n, 2n)^{13}\text{N}$ induced by irradiating the samples with 14 MeV neutrons, produced in a neutron generator. The ^{13}N product radionuclide decays via positron emission with a half-life of 9.96 min. The nitrogen content is then determined by counting the 511 keV positron-annihilation gamma-rays. However, the problem with this method is that, in some complex samples, some induced activities, which also emit positrons, contribute to the 511 keV activity measured. The relevant reaction interferences and their corrections have been discussed elsewhere (Ndiokwere & Jerabek, 1983) and will only be applied to the present analysis.

Investigations into the protein and mineral contents of Nigerian foodstuffs have been scanty. Oyenuga (1968) has studied the nutritive value of some Nigerian foodstuffs. Gill *et al.* (1980) examined a large number of Nigerian legumes for the presence of starch, protein, fats and oils and, most recently, Ndiokwere (1982) analysed some edible legumes for protein. It is known that in plant breeding research, proof of quality can be determined through analysis for the protein content of grains (Srapenyants *et al.*, 1976). Also, in agrochemical studies, knowledge of the concentrations of N, P and K, as well as other macronutrient elements, is important. The present study is therefore aimed at evaluating the crude protein and important mineral contents of various Nigerian foodstuffs and updating any available information on their nutritive values.

EXPERIMENTAL PROCEDURE

Sample preparation

Representative foodstuffs from each category, as shown in Table 1, were obtained from different markets in Nigeria. In some cases, the samples were air-dried for several days and ground. The samples of cassava, cocoyam and yam species, which were analysed wet, were peeled, finely sliced and packed into irradiation vials. The cocoyam and yam samples were harvested and preserved for about 6 months prior to analysis. The processed foodstuffs were used as purchased for analysis.

Diphenylamine (8.3% nitrogen), benzoic acid (26.6% oxygen) and salts or oxides of the metals, dissolved in nitric acid, were used as standards for the determination of nitrogen, oxygen and metal concentrations,

TABLE 1
Samples of the Nigerian Foodstuffs Analysed

<i>Foodstuff</i>	<i>Common and/or scientific names</i>	<i>Remarks</i>
FS.1	Cassava (<i>Manihot esculenta</i> Crantz)	
a	Roots peeled	Soaked in water, prepared as food in various ways
b	Roots peeled, grated and fried	Usually eaten as <i>gari</i>
c	Processed cassava flour	Sold as <i>cassavita</i> , peeled, dried and ground
FS.2	Cocoyam (<i>Xanthosoma mafaffa</i> Schott)	
a	Tuber peeled, white (Tannia)	Edible portion cooked or roasted.
b	Tuber peeled, white (Taro)	Edible portion cooked and eaten as food or used in thickening local soups
FS.3	a Yam (<i>Dioscorea rotundata</i> Poir) White, tuber peeled	Cooked and/or made into thick purée, also fried or roasted
b	Water Yam (<i>Dioscorea alata</i> L.)	Cooked or roasted
c	Yam (<i>Dioscorea cayenensis</i> Lam.) Yellow, tuber peeled	Cooked and/or made into thick purée
d	Processed yam flour	Prepared in hot water as pasty substance
FS.4	Rice (<i>Oryza sativa</i> L.)	
a	Brown grains	Locally grown
b	Long grains, parboiled	Imported
c	White, polished	Imported
d	Processed rice flour, white	Sold as ground rice, prepared in hot water as thick purée
FS.5	Plantains (<i>Musa paradisiaca</i> L.)	
a	Ripe, peeled	Usually sliced and fried
b	Unripe, peeled	Roasted, cooked or fried
c	Unripe, peeled, dried and ground	Plantain flour, also mixed with yam flour
FS.6	African breadfruit (<i>Treculia africana</i> Decne), seeds shelled	Cooked and flavoured as food, sometimes roasted
FS.7	Maize (<i>Zea mays</i> L.)	
a	Yellow grains	
b	White grains	
FS.8	Guinea Corn (<i>Sorghum bicolor</i> (L.) Moench) Grains	
FS.9	Millet (<i>Pennisetum glaucum</i> auct.) Grains	

(continued)

TABLE 1—contd.

Foodstuff	Common and/or scientific names	Remarks
FS.10	Cocoa Bean seeds (<i>Theobroma cacao</i> L.)	Used in preparing beverages
FS.11	Melon seeds (<i>Citrullus vulgaris</i> schrad.) Seeds shelled	Generally very popular condiment in local soups and stew
FS.12	Cotton seeds (<i>Gossypium</i> spp. L.)	Ground seeds used as condiment in local soups
FS.13	Bitter Kola nuts (<i>Circinia kola</i> heckel)	
a	Nuts light, yellowish	Mainly from northern Nigeria
b	Nuts reddish/brownish, violet	Mainly from Southern Nigeria
FS.14	Fish meal, ground	Dried crayfish/shrimps
FS.15	Stockfish, fleshy part, dried and ground	
FS.16	Pumpkin (<i>Telfairia occidentalis</i> Hook. fil.) Green leaves	Very popular vegetable, usually cooked
FS.17	Bitter Leaf (<i>Veronia amygdalina</i> Del.) green leaves	Popular vegetable, bitter taste is reduced by physical extraction with water before use

respectively. For nitrogen and oxygen determination the samples and standards were firmly packed into special polyethylene vials, accurately weighed by difference and heat sealed. About 5 g each of the food samples were used for the analysis. Firm packing of samples and standards was necessary to ensure a minimum of trapped air in the vials.

Irradiation and counting

Each sample and standard were exposed to 14 MeV neutrons produced by the Kaman A-711 sealed-tube generator at a flux of about 2×10^{11} n/s for 5 min. The 511 keV positron-annihilation gamma-rays associated with the decay of ^{13}N were counted for 10 min after a decay time of 11 min with a 7.5×7.5 cm NaI(Tl) scintillation counter. Oxygen was determined on the basis of the nuclear reaction $^{16}\text{O}(n,p)^{16}\text{N}$ by irradiating the sample and standard for 20 s and counting, after allowing it to decay for 20 s (the 6.13 and 7.12 MeV spectral regions for gamma-rays emitted by 7.1-s half-life ^{16}N for 20 s). The automated dual-activation facility

(Kaman A-711 neutron generator and counting system) of the University of California, Irvine, has been described elsewhere (Ndiokwere & Jerabek, 1983). Each sample and standard were then reversed and again irradiated and counted under the same conditions. The net photopeak counts for sample and standard in each case were normalized and summed to give the total counts for sample and standard, respectively. From the results, the 'apparent' nitrogen and oxygen concentrations were calculated.

In addition, phosphorus concentrations in the food samples were measured using the FNAA method, which is based on the $^{31}\text{P}(n, \alpha)^{28}\text{Al}$ reaction (half-life = 2.31 min, gamma-ray energy = 1778.9 keV). $\text{Ca}_3(\text{PO}_4)_2$ was used as the standard in this case. Interferences in phosphorus determination can occur due to the production of ^{28}Al , mainly from the reaction $^{28}\text{Si}(n, p)^{28}\text{Al}$. This interference is negligible, since silicon is usually present in these foodstuffs at trace levels. Of the foods analysed, sorghum grains have the highest silicon content (up to 0.076% Si) which could, however, interfere with the 0.083% P found.

The Ca, K and Fe concentrations in the food samples were also measured by thermal-neutron activation analysis under the following conditions:

- (a) For K and Fe:
neutron flux, $\phi = 1 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$; irradiation time, $t_i = 3 \text{ h}$;
decay time, $t_d = 12 \text{ h} - 14 \text{ days}$; counting time, $t_c = 10 \text{ min} - 60 \text{ min}$.
- (b) For Ca, using the pneumatic transfer facility of the reactor,
 $\phi = 2.5 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$, $t_i = 2 \text{ min}$, $t_d = 3 \text{ min}$ and $t_c = 3 \text{ min}$.
- (c)

	<i>Half-life, $T_{1/2}$</i>	<i>Measured gamma-ray energy (keV)</i>
^{49}Ca	8.8 min	3083
^{42}K	12.52 h	1524.7
^{59}Fe	45.1 days	1098.6 and 1291.5

The product of the percentage concentration of each element and the corresponding correction factor (Table 2) gave the percentage interference of the element in each food sample. Finally, the 'true' percentage nitrogen content of each sample was the difference between the 'apparent' percentage nitrogen and the total percentage interference of the elements Fe, K, O and P.

TABLE 2
Correction Factors for Iron, Oxygen, Phosphorus and Potassium in Nitrogen Determination (Ndiokwere & Jerabek, 1983)

<i>Element</i>	<i>Reaction interference</i>	<i>Correction factor</i> (<i>'apparent' percentage N/percentage element</i>)
Fe	$^{54}\text{Fe}(n, 2n)^{53}\text{Fe}$	0.03 ± 0.0004
O	$^{16}\text{O}(p, \alpha)^{13}\text{N}$	0.0068 ± 0.0001
P	$^{31}\text{P}(n, 2n)^{30}\text{P}$	0.09 ± 0.001
K	$^{39}\text{K}(n, 2n)^{38}\text{K}$	0.16 ± 0.002

RESULTS AND DISCUSSION

The results of the analysis for Ca, K, Fe and P in the foods are presented in Table 3. The concentrations are average values of two replicate measurements. The K and P concentrations are high for most food samples and range from 0.014% to 1.76% and 0.023 to 2.53%, respectively. The Fe concentrations are generally less than 0.04%. Similar trends are observed for Ca concentrations except for the foodstuffs FS.12 and FS.14–FS.17 in which the concentrations vary in the range 0.176% to 1.04%.

Knowledge of the approximate oxygen content of each foodstuff was required to evaluate the contribution due to the $^{16}\text{O}(p, \alpha)^{13}\text{N}$ knock-on, proton-induced reaction, which produces the same radionuclide, ^{13}N , as the desired reaction $^{14}\text{N}(n, 2n)^{13}\text{N}$. The oxygen content of the foodstuffs (not shown in Table 3) varied in the range 14.3%–33.7% and, with a correction factor, 0.0068, for oxygen, the contribution from this reaction interference is between 0.1% and 0.23%. This is not surprising when it is considered that most of these foodstuffs are mainly composed of cellulose, starch, sugar (as $\text{C}_6\text{H}_{12}\text{O}_6$), fats and proteins, which have a relatively low oxygen content.

The 'true' nitrogen values obtained in this work are presented in Table 4 and were converted to percentage crude protein using the Kjeldahl factor, 6.25. The protein values vary widely from 1.46% (FS.1) to 81.1% (FS.15). Except for the lowest 'apparent' nitrogen content of the foodstuffs cassava, cocoyam, yam, plantains and bitter kola nuts (Table 4), the standard deviations (1σ) of the means for four replicate determinations are in the range ± 2.1 to $+4.63$, relative, over the range 1.04% to 1.96%

TABLE 3
 Concentrations of Calcium, Iron, Phosphorus and Potassium in
 Various Nigerian Foodstuffs (Per cent Dry Weight, Unless
 Otherwise Indicated)

<i>Foodstuff</i>		<i>Ca</i>	<i>Fe</i>	<i>K</i>	<i>P</i>
FS.1	a*	0.014	0.000 1	0.346	0.051
	b	0.005	0.000 1	0.087	0.023
	c	0.011	0.000 1	0.291	0.047
FS.2	a*	0.008	0.001 2	0.014	0.472
	b*	0.051	0.001 7	0.026	0.36
FS.3	a*	0.065	0.001	0.021	0.083
	b*	0.024	0.000 7	0.035	0.051
	c*	0.018	0.001 4	0.027	0.077
FS.4	d	0.006	0.000 4	0.018	0.048
	a	0.014	0.003	0.373	0.34
	b	0.005	0.001	0.074	0.154
	c	0.007	0.001 3	0.212	0.17
FS.5	d	0.007	0.001	0.203	0.146
	a	0.034	0.001 3	0.141	0.044
	b	0.017	0.001	0.082	0.031
FS.6	c	0.015	0.001 2	0.076	0.03
		0.057	0.000 6	0.034	0.043
FS.7	a	0.007 4	0.003	0.54	0.464
	b	0.005	0.003 4	0.48	0.57
FS.8		0.034	0.000 4	0.412	0.083
FS.9		0.064	0.014	0.347	0.385
FS.10		0.176	0.016	0.28	0.843
FS.11		0.008	0.000 1	0.074	0.018
FS.12		0.204	0.000 1	0.384	0.87
FS.13	a	0.026	0.012	0.073	0.134
	b	0.041	0.021	0.084	0.154
FS.14		0.426	0.018	0.87	2.04
FS.15		0.74	0.032	1.24	2.53
FS.16		0.97	0.023	1.22	0.047
FS.17		1.04	0.014	1.76	0.035

* Foodstuffs not dried before analysis.

TABLE 4
 Nitrogen Concentrations and Calculated Crude Protein Content of Various Nigerian Foodstuffs (Per cent Dry Weight, Unless Otherwise Indicated)

Foodstuff	Per cent nitrogen 'apparent'	'True' per cent N	Crude protein ('True' per cent $N \times 6.26$)	Reported values
FS.1	a* 0.503 ± 0.028	0.443	2.77	2.58 (Oyenuga, 1968)
	b 0.25 ± 0.016	0.234	1.46	1.2 (Oyenuga, 1968)
	c 0.473 ± 0.03	0.422	2.64	
FS.2	a* 1.10 ± 0.057	1.05	6.56	5.87 (Oyenuga, 1968)
	b* 1.44 ± 0.091	1.4	8.75	7.57 (Oyenuga, 1968)
FS.3	a* 0.831 ± 0.052	0.82	5.13	4.42 (Oyenuga, 1963)
	b* 1.04 ± 0.074	1.03	6.44	7.26 (Oyenuga, 1968)
	c* 0.93 ± 0.051	0.92	5.75	5.44 (Oyenuga, 1968)
	d 0.7 ± 0.042	0.69	4.31	
FS.4	a 2.14 ± 0.11	2.05	12.8	12.51 (Oyenuga, 1968)
	b 1.73 ± 0.08	1.7	10.6	
	c 1.38 ± 0.072	1.33	8.31	9.1 (Oyenuga, 1968)
	d 1.19 ± 0.07	1.14	7.12	
FS.5	a 0.77 ± 0.035	0.74	4.63	3.71 (Oyenuga, 1968)
	b 1.0 ± 0.06	0.98	6.13	4.16 (Oyenuga, 1968)
	c 0.89 ± 0.042	0.875	5.47	
FS.6	2.48 ± 0.05	2.61	16.3	18.7 (Oyenuga, 1968)
FS.7	a 1.83 ± 0.07	1.7	10.6	10.65 (Oyenuga, 1968)
	b 1.96 ± 0.055	1.83	11.4	10.9 (Bibby & Champion, 1974)
FS.8	2.28 ± 0.06	2.21	13.8	15.03 (Oyenuga, 1968)
FS.9	1.76 ± 0.043	1.67	10.4	9.02 (Oyenuga, 1968)
FS.10	2.57 ± 0.063	2.45	15.3	14.28 (Oyenuga, 1968)
FS.11	5.06 ± 0.18	5.05	31.6	30.22 (Oyenuga, 1968)
				31 (Chuang <i>et al.</i> , 1977)
FS.12	4.60 ± 0.155	4.46	27.9	28.47 (Oyenuga, 1968)
FS.13	a 0.85 ± 0.054	0.821	5.13	4.27 (Oyenuga, 1968)
	b 0.72 ± 0.044	0.693	4.33	species not stated
FS.14	10.83 ± 0.25	10.5	65.5	65 (Bibby & Champion, 1974)
				66 (Chuang <i>et al.</i> , 1977)
FS.15	13.42 ± 0.38	13.0	81.1	84.3 (Oyenuga, 1968)
FS.16	4.034 ± 0.165	3.83	23.9	
FS.17	3.13 ± 0.14	2.84	17.8	

* Foodstuffs not dried before analysis (per cent wet weight).

'apparent', nitrogen. The relative error is much smaller for the higher 'apparent' nitrogen content (2.57–13.4%) foodstuffs. The reported nitrogen concentrations represent mean values from determination on two or more samples of a given foodstuff in most cases. For cassava, yam and cocoyam, several aliquots from a given sample were also analysed to check any possible variations within a sample. The results showed slight variations of 0.07% for cocoyam, 0.21% for yam and 0.03% for cassava.

The total percentage interference in the nitrogen determination in each sample was observed to be between about 0.01% and 0.4%. It is important to note that ^{30}P interference was considerably reduced by allowing a decay time of 11 min. This certainly had a negligible effect on the ^{13}N counting statistics.

In Table 4 the protein values of some foodstuffs reported by other workers are also given for comparison. The present results for some foodstuffs generally agree fairly well with the protein values reported by these authors. Discrepancies are, however, observed in most of the protein values for some foodstuffs reported by Oyenuga (1968).

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