ChemSearch Journal 8(2): 50 – 55, December, 2017
Publication of Chemical Society of Nigeria, Kano Chapter

Received: 03/11/2017 Accepted: 29/11/2017

Neutron Activation Analysis (NAA) and Energy Dispersive X-ray Fluorescence Analysis (EDXRF) on *Corchorus tridens* Linn

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ABSTRACT

Analyses were carried on *Corchorus tridens* Linn in order to ascertain its elemental composition using neutron activation analysis (NAA) and energy dispersive x-ray fluorescence analysis (EDXRF). Nineteen (19) of the detected and determined elements were either essential, trace or heavy (Al, Ba, Br, Ca, Co, Cr, Cu, Fe, Hf, K, La, Mn, Na Rb, Sm, Sc, Th, V and Zn) while ten (10) others (As, Cs, Dy, Eu, Lu, Mg, Ta, Ti, U and Yb) were found at below detection limit (BDL) levels. Variations of the elemental concentrations from the two techniques and the different parts of the plant were compared using student's t – test and ANOVA test. Translocation factor of the elements and their concentrations in the different parts of the plant were compared with normal concentrations in plants and recommended daily allowance (RDA) values. It was found that for some of the elements, pattern of distribution is in the order of roots > stems > leaves while for others there is no regular pattern of distribution. Also, the amounts of certain essential elements in C. *tridens* L. show that the plant can serve as a means of supplementation of required minerals for man and his animals.

Keywords: NAA, EDXRF, C. *tridens* L., translocation factor and bioaccumulation

INTRODUCTION

The plant *Corchorus tridens* Linn belongs to the family *Tiliaceae.* Its common names include turgunnuwa, or Lalo – Hausa/Fulani. The leaves and young shoots of the plant are used as a vegetable and soup herb, and are also a good fodder for camels and other domestic stock. It yields a good fiber which is used for fishing lines in northern Nigeria and elsewhere. When long, the stems are used for horizontal ties of conical hut roofs (Dalziel, 1955).

Phytochemical analysis of the *Corchorus* species to which C. *tridens* L. belongs indicates the presence of cardiac glycosides, triterpenes, ionones, phenolics, sterols, coumarins, steroids and fatty acids (Khan *et.al*, 2006) which are important components of plants used in traditional medicine.

The contribution of medicinal plants in traditional system of medicine for curing diseases has been well documented (Delang, 2007 and Hosseinzadeh *et.al*, 2015). Nowadays increased scientific interest and consumer demand have promoted the development of herbal products as dietary supplements (Khan e*t. al*, 2006). In view of the renewed interest, oriental herbal medicines have a prominent role to play in the pharmaceutical and health markets of the 21st century (CSIR, 1950). It has been reported that whatever is taken as food could cause metabolic disturbance subject to the allowed upper and lower limits of trace metals (Chopra *et.al*, 1958). Both the deficiency and excess of essential micronutrients and trace of toxic metals may cause serious effects on human health (Satyavati *et.al*, 1976 and Wahid and Siddiqui, 1961).The use of medicinal plants in therapeutics or as dietary supplements goes back beyond recorded history, but has increased substantially in the last decades (Bhatt *et.al*, 2003 and Sen, 1930). However, the safety of their use has recently been questioned due to the reports of illness and fatalities (Gupta and Raina, 1998). Medicinal herbs are easily contaminated during growth, development and processing. After collection and transformation in to dosage form the heavy metals confined in plants upon administration, they enter the human body and may disturb the normal functions of central nervous system, liver, lungs, heart, kidney and brain, leading to hypertension, abdominal pain, skin eruptions, intestinal ulcer and different types of cancers (Moscow and Jothivenkatachalam, 2012 and Jaishankar *et.al*, 2014).

For this study, the techniques of energy dispersive x-ray fluorescence (EDXRF) and neutron activation analysis (NAA) were used. The techniques have the advantage of being non destructive, multi-elemental, minimal sample preparation, fast, easy to use and cost effective (Win, 2004 and Moriyama, 2013). In EDXRF measurement, sample is subjected to an excitation

source of primary photons, such as x – ray tube that displaces electrons from the inner shells of atoms. On rearrangement of the electrons to return to a stable state, energy is released as radiation. These energy changes are in the x-ray part of the spectrum which can be used to detect the relative abundances of the elements that are present in the sample (Cesareo and Viezzoli, 1983). For neutron activation analysis (NAA), the technique is based on the principle that whenever neutrons impinge on the biological material, some of the neutrons are captured by most stable isotopes of constituent elements and transformed to radioactive isotopes. Then the activated nuclei decay according to their characteristic half-lives. Some nuclides emit beta (β) particles only, but most nuclides emit gamma (γ) quanta too, with specific energies. The quantity of radioactive nuclides is determined by measuring the intensity of the characteristic gamma ray in the spectra (Hailu *et.al*, 2012).

With this background, this work was under taken to determine the elemental composition of samples of C. *tridens* L. using EDXRF and NAA with the view of assessing its nutritional, therapeutic potentials or safety in relation to its use.

MATERIALS AND METHODS

Seventy five (75) samples of C. *tridens* L. materials (roots, stems, fruits and leaves) were collected from Karkari village, Gwarzo Local Government Area of western part of Kano State, Nigeria and transported in polyethene bags. The plant was identified at the Department of Biological Sciences of Ahmadu Bello University (ABU) Zaria where voucher specimens were kept.

Sample treatment

After collection, the samples were washed twice with tap water and rinsed with deionised water. They were first air dried for seven (7) days and then further dried in an oven at 60 ^{O}C for 12 hours. After drying, the samples were ground using pestle and mortar and passed through 125µm mesh sieve.

Neutron activation analysis measurement

Each ground sample was pulverized and approximately 150 mg was weighed and wrapped in polyethylene films. For the elements leading to short-lived activation products, the sample was packed and sealed in 7 cm^3 rabbit capsules. Irradiation with thermal neutrons was carried out at an outer irradiator channels (i.e., B_4) of the Nigeria Research Reactor-1 (NIRR-1) operating at a thermal neutron flux setting of 2×10 n/cm^{2}s, which corresponds to a neutron flux of 1×10 n/cm^{2}s in the outer channels. After the irradiation, a PCm - based gamma ray spectrometry set-up performed measurement of induced radionuclide. This consists of a HPGG detector coupled to a computer based Multi-Channel Analyzer (MCA) via electronic modules. The relative efficiency of the detector is 10 % and an energy resolution of 1.95 KeV at gamma-ray energy of 1332 KeV belonging to ^{60}Co was used. Through appropriate choice of cooling time, detector's dead time was controlled to be less than 10 %. Identification of gamma ray of product radio nuclides through their energies and quantitative analysis of their concentrations was achieved using the gamma ray spectrum analysis software, WINSPAN - 2004. The certified reference material IAEA – soil - 7 was used as the standard, while other two certified reference materials, GSD - II and GSR-5 were used as analytical quality control materials to validate the procedure for all the elements (Dim *et.al*, 2004, Jonah *et.al*, 2006, Gwarzo *et.al*, 2014).

Energy Dispersive X-ray Fluorescence Analysis Measurement

Approximately 0.5 g of each sample was measured and then poured in to a pelletizer (without a binder). A pressure of about 10 tonnes (204081 NM^{-2}) was applied to each sample during pelletization using the SPECAC hydraulic press. The pellets produced had dimensions of 2 mm in thickness and 25 mm in diameter. Each pellet was placed on the annular cadmium 109 isotopic excitation source which sits directly on the lithium drifted selenium detector (Se (Li)) with a barium window. Underneath the detector is the liquid Nitrogen Dewar, which produces cooling effect on the detector of the spectrometer.

Translocation factor

Translocation factor (TF) or mobilization ratio establishes pattern of translocation metals from roots to other parts of the plant species and is useful in monitoring of heavy metal contamination as well as selection of metal accumulators or tolerant species. The metal translocation process in plant species is a crucial factor in determining the metal distribution in different tissues (Singh *et.al*, 2010). A number of factors including anatomical, biochemical and physiological factors contribute to metal accumulation and distribution in upper vegetative parts of plants. It is computed as:

$$Translocation\ factor = \frac{Concentration\ of\ element\ in\ \ vegetative\ part\ of\ the\ plant}{Concentrtion\ of\ element\ in\ soil/\ root}$$

In this work, two kinds of translocation factor were computed; from roots to the stems ($T_{S/R}$) and from the stems to the leaves ($T_{S/L}$). Its values will enable us to declare the plant as either hyperaccumulator, accumulator or excluder (Gupta *et. al*., 2008).

RESULTS AND DISCUSSIONS

Table 1 indicates the results and standard deviations of the elemental analysis of different parts of the C. *tridens* L. sample as determined by NAA and EDXRF techniques (analyses were carried out in triplicates). Statistical analysis (t – test and ANOVA) on the results indicated that, for some of the elements (Ba, Ca, Fe, K, Mn and V) there was no significant difference in their concentrations using the two techniques and in the different parts of the plant for (Al, Br, Co, La, Rb, Sm, Th and Zn). Significant differences were observed at $p \leq 0.5$ for Ba, Ca, Cr, Sc, Na and V in the different parts of the plant analyzed. This is attributed to the capability of the plant to bioaccumulate some of these elements in its different organs while differences in the concentrations of some the metals in the same samples and measured by the different methods may be attributed by the accuracy, precision and capabilities of the two techniques used (Goulden, 1978).

The concentration of major elements including K and Ca is generally known to be in high in tissues of plants, because of the roles they play as components of simple salts and complexes performing various functions (Yalwa, 2002). However, their concentrations in the analyzed plant samples (8985 – 54290 ppm and 3788 – 17765 ppm) are relatively higher than normal concentrations found in most plants (10 – 100 ppm and 50 – 60 ppm) (Allen *et.al*, 1974).

For elements such as Ba, Fe, Mn, Zn, Rb and Co, their concentrations were also high and in fact some values of the elements such as Fe (376 – 8945 ppm), 8.825 – 138.0 ppm (Ba), 23.0 – 496.224 ppm (Mn), 14.0 – 51.0 ppm (Zn), 3.9 – 23.0 ppm (Rb), and 0.00 – 0.41 ppm (Co) indicate that C. *tridens* L. is an indispensable sources of micronutrients to man and his animals when consumed. This is because the normal concentrations of these metals in plants are Fe (40.0 – 500.0 ppm), Ba (9.2 – 131.9 ppm in Sedge and Nutgrass), Mn (50.0 – 356.0 ppm), Zn (15.0 – 100.0 ppm), Rb (0.2 – 194.0 ppm), and Co (0.1 – 0.60 ppm) and the above values of the metals determined are within normal range.

Moreover, for the ultra-trace elements; Sc, Sm, Th, Br, V, La, Cu, Sb, Lu and Eu, their concentrations are relatively within normal levels. This is evident when concentrations of these elements in this study are compared to normal levels in plants. For example, the range of Sc concentration in *C. tridens* L. was 0.03 – 0.95 ppm while its normal range in vegetables is 5.00 ppb and 70.0 ppb in grasses. Sm in this study was found to be 0.03 – 0.06ppm while 0.11– 0.12 ppm was found by Zhang *et al.*, 2013. Also Th was found to be 1.1ppm while the normal range in plants is $2.0x10^{-3}$ – $3.6x10^{-3}$ Ci/g, V found in this study was 0.7 – 73.309 ppm while its normal range in plants is 96.0 – 112.0 ppm which signifies low concentration of the element in the analyzed plant. For La however, the range was 0.034 – 2.72 ppm while its normal range in plants is generally low (Wang *et al.*, 1997). In addition to that, the concentration range of Cu found in this study was 22.457 – 114.885 ppm being higher than normal concentrations (10.0ppm) of the element in plants (Yruela, 2005).

Table 1: Concentration of the determined elements in the leaf, stem and root of C. *tridens* L. using NAA and EDXRF techniques

Sample	Leaf (CTLL)		Stem (CTLS)		Root (CTLR)	
Element	*NAA*	EDXRF	NAA	EDXRF	NAA	EDXRF
Al	1453.0±119.0†	Nd	209±19.0	Nd	334±29.0†	Nd
As	BDL	Nd	BDL	Nd	BDL	Nd
Ba*	138.0±19.0[a]†	8.825±2.1[a]	111.0±18.0‡	Nd	BDL	Nd
Br	5.0±1.0†	Nd	3.5±0.6	Nd	BDL	Nd
Ca*	14750.0±2139.0[a]‡	17765.0±374.0[a]	12350.0±1803.0‡	Nd	3788.0±591.0†	Nd
Co	0.46±0.11†	Nd	0.36±0.12†	Nd	BDL	Nd
Cr*	3.48±1.02[a]	60.361±9.6[a]‡	BDL	78.585±9.12‡	BDL	79.742±18.4‡
CS	BDL	Nd	BDL	Nd	BDL	Nd
Cu	Nd	114.885±11.2†	Nd	32.274±2.14†	Nd	22.457±13.7†
Dy	BDL	Nd	Nd	BDL	Nd	Nd
Eu	BDL	Nd	BDL	Nd	NdA	Nd
Fe*	1130.0±73.0	8945.0±89.34[a]‡	BDL	8005.0±167.0‡	376.0±45.0[a]	8410.0±194.6[a]‡
Hf	1.9±0.1	Nd	BDL	Nd	Nd	Nd
K*	43120.0±517.0[a]	21590.0±1884.3a	54290.0±326.0[a]‡	13210.0±349.5[a]‡	21110.0±1457.0[a]	8985.0±158.5[a]‡
La	2.72±0.04	Nd	0.034±0.002	Nd	1.7±0.1†	Nd
Lu	BDL	Nd	BDL	Nd	BDL	Nd
Mn*	62.3±2.6[a]	496.224±39.3[a]‡	32.0±1.0[a]	234.76±15.7[a]‡	23.0±1.0[a]	196.92±25.2[a]‡
Na	416.0±3.0‡	Nd	198.0±2.0‡	Nd	315.0±180.0‡	Nd
Rb	23.0±2.0†	Nd	20.0±3.0†	Nd	3.9±0.8†	Nd
Sb	BDL	Nd	BDL	Nd	BDL	Nd
Sc	0.33±0.01	Nd	0.043±0.008	Nd	0.11±0.01‡	Nd
Sm	BDL	Nd	BDL	Nd	Nd	Nd
Ta	1.1±0.1†	Nd	BDL	Nd	BDL	Nd
Th	BDL	Nd	BDL	Nd	BDL	Nd
Ti	BDL	Nd	BDL	Nd	BDL	Nd
U	BDL	Nd	BDL	Nd	0.7±0.2[a]	Nd
V*	1.9±0.30	64.489±4.9[a]‡	BDL	88.545±7.34‡	BDL	73.309±5.3[a]‡
Yb	BDL	Nd	BDL	Nd	BDL	Nd
Zn	51.0±4.0	Nd	22.0±3.0†	Nd	14.0±3.0	Nd

BDL means below detection limit; Nd; Not determined;* elements determined by INAA and EDXRF; superscript [a], are not significantly different at $p > 0.05$. † Elements determined in the parts of C. *tridens* L. are not significantly different while ‡ are significantly different at $p > 0.05$.

Since the motive for elemental analysis of green plants, food and feed samples is mainly aimed to investigate nutritional quality or contamination, one of the indices for such is transfer factor (TF). In this study the TF has been categorized as either $TF_{Shoot/Root}$ ($TF_{S/R}$) or $TF_{Shoot/Leaf}$ ($TF_{S/L}$). Most plant species have been found to have TF >1. For Al, the $TF_{S/R}$ for *C. tridens* Linn (1.59), was determined and signifies good transfer of the element from roots to shoots, while $TF_{L/S}$ was found to be <1 indicating accumulation of the element in the stems of the plant.

However, the TF values for Ba, Ca, K, La, Mn, Na, Rb and Zn in C. *tridens* L. varied in a similar manner to that found for Al discussed earlier. $TF_{S/R}$ values of those elements that were >1 ranged 1.59 – 50.0 while those that were <1 ranged between 0.31 – 0.64 as shown in Table 2. $TF_{L/S}$ values for the aforementioned elements were all <1 except for K and Zn as indicated in table 2. The implications of this finding are that, C. *tridens* L. absorbs most of the metals and bioaccumulate them in the stems ($T_{S/R} \geq 1$) which are normally not edible leaving the leaves with moderate concentrations ($T_{S/R} \leq 1$) and suitable for human consumption (Mirecki *et.al*, 2015).

Table 2: Translocation factors of some of the elements determined between the roots to the stems ($T_{S/R}$) and stems to the leaves ($T_{L/S}$) of C. *tridens* Linn.

Translocation factor	Al	Ca	K	La	Mn	Na	Rb	Sc	Zn
$T_{S/R}$	1.59	0.31	0.39	50.0	0.72	1.59	0.20	2.56	0.64
$T_{L/S}$	0.14	0.84	1.26	0.01	0.51	0.48	0.87	0.31	2.32

CONCLUSION

This study was conducted in order to ascertain the elemental composition in the different parts of C. *tridens* L. and their transfer factors. Essential elements were found to be at high concentrations and compares well with the exotic vegetables. This indicates that the plant can contribute to the diet of individuals that may consume it at appropriate concentrations. The presence of toxic metals at low concentrations or BDL levels in the plant is a further account of this claim. Also the values of the translocation factor (mostly < 1) indicates that C. *tridens* L. the plant cannot be a hyperaccumulator of any of the determined elements probably with the exception of La ($T_{S/R}$ = 50) which hyper accumulate the metal in its stems.

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