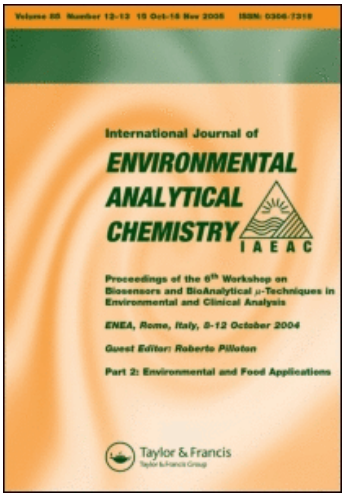


International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

# Dry-Ashing Preconcentration for Micro-Reactor-Based Neutron Activation Analysis of Food and Plant Samples

Gerald C. Lalor[a]; Percy C. Onianwa[a]; Mitko K. Vutchkov[a]
[a] International Centre for Environmental and Nuclear Sciences, University of the West Indies Mona, Kingston 7, Jamaica

Online publication date: 17 September 2010

**To cite this Article** Lalor, Gerald C. , Onianwa, Percy C. and Vutchkov, Mitko K.(2003) 'Dry-Ashing Preconcentration for Micro-Reactor-Based Neutron Activation Analysis of Food and Plant Samples', International Journal of Environmental Analytical Chemistry, 83: 5, 367 — 374
**To link to this Article: DOI:** 10.1080/0306731031000104740
**URL:** http://dx.doi.org/10.1080/0306731031000104740

*Intern. J. Environ. Anal. Chem.*, Vol. 83, No. 5, pp. 367–374



# DRY-ASHING PRECONCENTRATION FOR MICRO-REACTOR-BASED NEUTRON ACTIVATION ANALYSIS OF FOOD AND PLANT SAMPLES

GERALD C. LALOR*, PERCY C. ONIANWA† and MITKO K. VUTCHKOV

*International Centre for Environmental and Nuclear Sciences, University of the West Indies, Mona, Kingston 7, Jamaica*



*(Received 17 October 2002; in final form 16 February 2003)*

The application of preconcentration by dry-ashing to the neutron activation analysis of biological samples using a SLOWPOKE-2 low-power reactor is reported. Samples of selected food crops (banana, callaloo, carrot, mango, and yam) and bioindicator plants (lichen, moss, *Tillandsia* sp., and tree bark) were analysed both as plant tissue, and as ashed sample. The results are presented for 21 elements. Good agreement between both procedures (< 10% relative standard error) was obtained for 13 elements: Al, Ca, Cd, Cr, Fe, K, La, Mg, Mn, Na, Sm, Ti, and V. For Dy, Rb, and Zn the agreement was 10–15%. Relatively poorer agreement (> 15–30%) was obtained for As, Br, Cl, and Sb. Dry ashing produced improved analytical results for those samples that were of low ash content. However, the increased background counts observed in ashed samples can sometimes negate the concentration gain, particularly in plants with high ash contents but low levels of certain elements.

*Keywords:* Dry ashing; Preconcentration; Neutron activation analysis; Low-power reactor; SLOWPOKE-2

## INTRODUCTION

Concerns about nutrition and the occurrence of potentially hazardous elements in the environment have led to the development of often stringent guidelines and regulations for food and environmental quality. Analysis of such foods and environmental samples often requires sophisticated analytical tools with the capacity to meet requirements for high accuracy, low detection limits, and reasonably high throughput rates.

The increasing use of micro-reactors, with their advantages of stability, simplicity, and low operational costs, makes the use of Neutron Activation Analysis (NAA) potentially attractive in these applications. However, these small reactors, such as the SLOWPOKE-2, are limited by their typical maximum operational neutron flux of $10^{12}\,n\,cm^{-2}\,s^{-1}$, and continuous irradiation times of only about 8 h at full flux. This

*Corresponding author. Fax: +876 977-0768. E-mail: glalor@uwimona.edu.jm
†TWAS Visiting Research Fellow. Present address: Department of Chemistry, University of Ibadan, Ibadan, Nigeria.

ISSN 0306-7319 print: ISSN 1029-0397 online © 2003 Taylor & Francis Ltd
DOI: 10.1080/0306731031000104740

means that the attainable detection limits are frequently too high for many elements of interest at the low concentrations that frequently occur in biological matrices. While radiochemical separations can improve the analytical sensitivity, they add an unwelcome dimension of complexity and require other specialised facilities. Preconcentration by dry ashing can be useful because most biological materials have high mass-reduction factors when ashed since they are comprised mainly of combustible organic matter. However, some volatile elements may be lost during ashing while some elements may be incorporated into the container wall at high temperatures [1–6]. For many elements such losses can be minimised to tolerable levels at temperatures of 450–500°C [3,5,7]. The limitation of the dry-ashing technique applied to NAA has not been sufficiently reported in the literature as is the case with applications to other analysis methods such as atomic absorption spectrophotometry. Reports on dry ashing for NAA have so far only dealt with a limited number of elements and biological sample types [1,4,8–12].

This article examines the use of micro-reactor based NAA for analysis of foods and bioindicator plants after preconcentration by dry-ashing. The specific reactor in use here is the SLOWPOKE-2.



## MATERIALS AND METHODS

### Samples and Standards

The food samples examined, banana, callaloo, yam, carrot, and mango were grown in central Jamaica. Rice is imported and was purchased on the open market. The bioindicators, moss, lichen, *Tillandsia* sp. (epiphytic 'spanish ball'), and the bark of the *Sandbox* tree, were also obtained from central Jamaica. These species have been used in pollution monitoring [13–15].

The samples were thoroughly cleaned to remove adhered soil and washed with distilled–deionised water. Edible portions of the foods were used. The cleaned samples were dried in an oven at 50°C for 2 days, and ground in an agate mortar. Freezing with liquid nitrogen facilitated the grinding of the *Tillandsia* and moss samples. Each ground sample was split into two portions, one of which was analysed directly. The other was ashed in a programmed-temperature muffle furnace set to attain 450°C in 2 h and to maintain this for 24 h. Standard Reference Material (NIST) 1573a Tomato Leaves and 1633a Coal Fly Ash were used for analytical quality assessment.

For neutron activation analysis about 400 mg of plant tissue or ash sample was weighed into a 25 mm × 25 mm polyethylene bag and heat-sealed. For long-irradiations about 1000 mg sample was weighed into 1.5 cc polythene capsule and heat-sealed. The standard reference materials used for Quality Control were dried for 2 h at 85°C for moisture determination and prepared in the same way as the samples. Single comparator standards, prepared by pipetting aliquots of standard solutions (SPEX CERTIPREP) onto Whatman No. 41 filter paper, were used for derivation of the activation constants used in calculating the elemental concentrations [16].

### Irradiation, Counting and Data Processing

The samples and standards were irradiated using the in-core irradiation sites of the SLOWPOKE-2 reactor. For the shorter-lived radioisotopes a 5-min irradiation at a

neutron flux of $5 \times 10^{11}$ n cm$^{-2}$ s$^{-1}$ was used. The samples were counted after decay times of 5 min and 30 min. To measure longer-lived nuclides, the samples were irradiated for 4 h at a flux of $10^{12}$ n cm$^{-2}$ s$^{-1}$, cooled for 5 days then counted for medium-lived elements. The long-lived elements were counted in the samples after 21 days.

The counting systems consisted of an EG&G ORTEC Gamma X hyperpure Ge detector with a resolution of 1.90 keV for the peak of 1332 keV of $^{60}$Co and a CANBERRA Reverse Electrode Ge detector with associated pulse processing electronics. Gamma ray spectrum analysis and quantification was carried out using EG&G ORTEC's OMNIGAM package. Statistical analysis of the results was carried out using the Jandel SigmaStat 2.0 package.

## RESULTS AND DISCUSSION

A comparison of the results obtained with the certified values for the plant and ash standard reference materials – SRMs 1573a Tomato Leaves, and 1633a Coal Fly Ash is in Table I. The agreement is within $\pm 10\%$ for most of the elements. Cu and V levels in the reference plant material were, however, below the detection limits for our procedure. The detection limits were estimated from the background count rates at the base of the analyte peak using the $3\sigma$ criterion.

The ash contents of the various food and plant samples are shown in Table II. Ashing was not complete for the rice sample at 450°C; although, a very significant reduction in the mass of carbonaceous matter was obtained. Complete ashing of rice would have required a higher temperature at which volatility losses might be appreciable for many elements. Complete organic matter destruction is not a critical requirement for the application of dry ashing to NAA because the results are always related to

TABLE I NAA results (μg g$^{-1}$) for tomato leaves SRM 1573a and coal fly ash SRM 1633a

| *Element* | *Tomato leaves SRM 1573a* | | *Coal fly ash SRM 1633a* | |
|---|---|---|---|---|
| | *This study* | *Certified value* | *This study* | *Certified value* |
| Al | 621 | 598 ± 12 | 146 300 | 143 990 |
| As | 0.14 | 0.112 | 156 | 145 ± 15 |
| Br | 1540 | 1300 | 2.40 | 2.3 |
| Cd | 1.86 | 1.52 ± 0.04 | 1.42 | 1.0 ± 0.15 |
| Cl | 6340 | 6600 | n.d. | – |
| Co | 1.59 | 0.57 ± 0.02 | 48 | 46 |
| Cr | 1.68 | 1.59 ± 0.06 | 206 | 196 ± 6 |
| Cu | n.d. | 4.7 ± 0.14 | 111 | 118 ± 3 |
| Fe | 416 | 368 ± 7 | 95 090 | 94 000 ± 1000 |
| K | 25 900 | 27 000 ± 500 | 17 600 | 18 790 ± 600 |
| La | 2.19 | 2.3 | 88 | 83 ± 3 |
| Mg | 10 840 | 12 000 | 4700 | 4550 ± 10 |
| Mn | 252 | 246 ± 8 | 182 | 190 |
| Na | 127 | 136 ± 4 | 1780 | 1700 ± 100 |
| Ni | n.d. | 1.59 ± 0.07 | 135 | 127 ± 4 |
| Rb | 16.0 | 14.89 ± 0.27 | 158 | 131 ± 2 |
| Sc | 0.11 | 0.1 | 40.2 | 40 |
| Sm | 0.20 | 0.19 | 16.1 | 17 ± 2 |
| V | n.d. | 0.835 ± 0.010 | 265 | 300 |
| Zn | 33.7 | 30.9 ± 0.7 | 254 | 220 ± 10 |

n.d. = not detected.

TABLE II Ash contents of the analysed samples

| *Food crops* | | *Other plants* | |
|---|---|---|---|
| *Sample* | *Ash content* (%) | *Sample* | *Ash content* (%) |
| Rice | 0.6 | Lichen | 3.7 |
| Yam | 1.2 | Moss | 8.1 |
| Mango | 2.2 | *Tillandsia* | 8.8 |
| Banana | 4.7 | Tree bark | 13.0 |
| Carrot | 14.8 | SRM1573a (tomato leaves) | 21.3 |
| Callaloo | 25.3 | | |

TABLE III Results (μg $g^{-1}$) of triplicate analysis of a yam sample direct and after ashing

| *Element* | *Plant tissue analysis* | | | | *Ashed sample analysis* | | | |
|---|---|---|---|---|---|---|---|---|
| | *S1* | *S2* | *S3* | *C.V* (%) | *A1* | *A2* | *A3* | *C.V.* (%) |
| Al | 18.3 | 14.2 | 17.7 | 13.3 | 17.5 | 16.7 | 17.3 | 2.2 |
| Br | 2.99 | 2.94 | 2.78 | 3.8 | 2.86 | 2.9 | 2.89 | 0.7 |
| Ca | n.d | 284 | n.d. | – | 235 | 226 | 188 | 11.6 |
| Cd | 0.7 | 0.43 | 0.4 | 32.4 | 0.32 | 0.4 | 0.39 | 11.8 |
| Cl | 1060 | 984 | 1070 | 4.5 | 963 | 791 | 981 | 11.5 |
| Cu | n.d. | n.d. | n.d. | – | 6.00 | 6.49 | 6.22 | 3.9 |
| Fe | n.d. | n.d. | n.d. | – | 25.4 | 18.2 | 24.8 | 17.5 |
| K | 11 700 | 11 670 | 11 900 | 1.1 | 11 300 | 12 500 | 11 300 | 5.9 |
| Mg | 363 | 675 | 390 | 36.3 | 389 | 384 | 407 | 3.1 |
| Mn | 1.71 | 1.6 | 1.69 | 3.5 | 0.98 | 1.22 | 0.92 | 15.3 |
| Na | 44.1 | 36.2 | 39.3 | 10.0 | 47.9 | 43.8 | 45.7 | 4.5 |
| Rb | 3.1 | n.d. | n.d. | – | 4.04 | 4.14 | 4.10 | 1.2 |
| Sm | 0.02 | 0.02 | 0.01 | 28.6 | n.d. | n.d. | n.d. | – |
| Zn | n.d. | n.d. | n.d. | – | 9.59 | 10.2 | 9.56 | 3.7 |
| *Mean C.V.* (%): | | | 17.0 | | | | | 4.9 |
| *Median C.V.* (%): | | | 11.6 | | | | | 4.5 |

C.V. = coefficient of variation; n.d = not detected.



the original sample mass. A good degree of mass reduction is, however, necessary to make the application of dry ashing useful. The ash contents of rice, banana, mango, and yam are below 5% indicating the value of the preconcentration step in the analysis of these foods because the resulting high mass-reduction factors provide higher degrees of amplification of the elements in the ash. High ash contents were found in carrot, callaloo, moss, *Tillandsia*, and tree bark. This indicates that many elements will be present at concentrations in the plant tissue, which are directly determinable. Given the low mass-reduction factors derivable from these, dry ashing may not be much required for determining many elements in these materials.

The precision of the results obtained by triplicate analyses of a sample of yam before and after ashing are compared in Table III. The concentrations reported for ashed sample analyses were corrected to plant sample values through dividing the concentrations in the ash by the respective mass-reduction factors, i.e. the sample/ash mass ratios. With the exception of Cl, K, and Mn, the precision obtained for the ashed samples was better than for the unashed plant. The very poor coefficients of variation observed for Cd, Mg, and Sm in the plant reflects the low concentrations therein. After ashing, the element concentrations in the irradiated sample are enhanced well above the detection limits, yielding better reproducibility.

Table IV gives the results of analyses for the food samples. Of the various elements that were determined the concentrations of Au, Ba, Ce, Eu, Hf, I, In, Lu, Nd, Sc, Sr, Th, and U were below the respective working detection limits for both procedures in all the samples. Twelve elements, Al, As, Br, Cl, Ca, Fe, K, Mg, Mn, Na, Rb, and Zn, were determinable in most of the food samples either by direct plant tissue analysis or after ashing. The levels were usually higher in callaloo and carrots than in the others. The concentrations of Dy, La, Sb, Sm, Ti, and V were measurable in few of the foods, and mainly after ashing in most of the samples. Detectable levels of Cu could be obtained in ashed samples of rice, mango, and yam.

The results for the bioindicator plants analysed are given in Table V. Concentrations of most elements in these plants were above detection limits for both procedures. The few exceptions include Cu, Sb, and Ti, which were measurable in fewer number of samples. Given the relatively high and measurable concentrations of many elements in moss, lichen, *Tillandsia*, and the food crops – carrot and callaloo – dry ashing may not be critical for determining most elements in these materials.

The relative standard errors between the results of the analysis of ash and plant tissue materials was evaluated for the samples listed in Tables IV and V. The medians and standard deviations of these relative errors for each element are plotted in Fig. 1. The results show that the elements may be categorised into three groups, based on the levels of agreement between the two procedures:

(a) Elements with < 10% relative standard error: these include some major and minor elements in plants, as well trace elements with high NAA sensitivities, i.e. Ca, Ti, Fe, Mn, Na, V, K, La, Mg, Sm, Cd, Cr, and Al.



TABLE IV Element concentrations (μg $g^{-1}$) in dry and ashed food samples

| *Element* | *Banana* | | *Rice* | | *Callaloo* | | *Carrot* | | *Mango* | | *Yam* | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *S* | *A* | *S* | *A* | *S* | *A* | *S* | *A* | *S* | *A* | *S* | *A* |
| Al | 24.2 | 16.5 | 14.8 | 8.7 | 1240 | 1106 | 1150 | 1064 | 20 | 14.8 | 17.1 | 12.6 |
| As | n.d. | n.d. | 0.21 | 0.18 | 0.15 | n.d. | n.d. | 0.3 | 0.09 | n.d. | 0.03 | 0.02 |
| Br | 9.01 | 6.28 | 13.9 | n.d. | 71.7 | 90.4 | 73.3 | 57.4 | 0.14 | 0.09 | 3.89 | 3.5 |
| Ca | n.d. | n.d. | n.d. | n.d. | 24 000 | 21 300 | 6960 | 6110 | 2640 | 2070 | n.d. | n.d. |
| Cd | n.d. | 0.57 | 0.47 | 0.39 | 0.42 | n.d. | 21.3 | 21.9 | 0.09 | 0.11 | 1.03 | 1.12 |
| Cl | 4340 | 3080 | 208 | n.d. | 9500 | 8650 | 2910 | 2360 | 1140 | 791 | n.d. | n.d. |
| Cr | 0.56 | n.d. | n.d. | n.d. | n.d. | 3.84 | 4.49 | 3.86 | n.d. | n.d. | n.d. | n.d. |
| Cu | n.d. | n.d. | n.d. | 2.17 | n.d. | n.d. | n.d. | n.d. | n.d. | 2.5 | n.d. | 3.85 |
| Dy | n.d. | n.d. | n.d. | n.d. | n.d. | 0.08 | 0.13 | 0.11 | n.d. | n.d. | n.d. | n.d. |
| Fe | 41.2 | 36.7 | n.d. | n.d. | 877 | 891 | 621 | 598 | 34.3 | 37.3 | n.d. | 16.9 |
| K | 17 400 | 16 900 | 1180 | 1070 | 76 700 | 69 600 | 47 000 | 49 400 | 8040 | 7120 | 7470 | 5290 |
| La | n.d. | n.d. | n.d. | n.d. | 0.74 | 0.67 | 1.13 | 1.22 | n.d. | n.d. | n.d. | 0.02 |
| Mg | 1980 | 1560 | n.d. | 411 | 7460 | 6690 | 2340 | 2050 | 1160 | 1080 | 397 | 418 |
| Mn | 11.3 | 8.84 | 10.8 | 11 | 88.5 | 79.1 | 45.6 | 38.4 | 11.6 | 10.5 | 1.18 | 1.19 |
| Na | n.d. | 15.8 | 15.7 | 17 | 629 | 566 | 1100 | 1020 | 24 | 19.7 | 38.9 | 30.2 |
| Rb | 3.81 | 4.9 | 3.9 | 3.5 | 74.9 | 72.3 | 9.1 | 11.2 | 5.1 | 4.4 | 7.73 | 6.99 |
| Sb | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.024 | 0.018 | 0.17 | 0.2 |
| Sm | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.3 | 0.26 | n.d. | n.d. | 0.01 | 0.01 |
| Ti | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 65.9 | 62.4 | n.d. | n.d. | n.d. | n.d. |
| V | n.d. | 0.18 | n.d. | n.d. | 2.14 | 1.88 | 3.1 | 3.02 | n.d. | n.d. | n.d. | n.d. |
| Zn | 12.2 | 10.9 | 36.9 | 31.7 | 50.4 | 54.6 | 48.4 | 52.5 | 11.4 | 9.3 | 14.5 | 11.3 |

S = sample concentrations obtained by direct plant tissue irradiation; A = sample concentrations derived from ashed samples analysis; n.d. = not detected.

TABLE V Element concentrations (μg $g^{-1}$) in dry and ashed plant samples

| *Element* | *Moss* | | *Lichen* | | Tillandsia *sp.* | | *Tree bark* | | *SRM 1573a (tomato leaves)* | |
|---|---|---|---|---|---|---|---|---|---|---|
| | *S* | *A* | *S* | *A* | *S* | *A* | *S* | *A* | *S* | *A* |
| Al | 4680 | 4826 | 1380 | 1352 | 535 | 583 | 158 | 137 | 621 | 635 |
| As | 1.02 | 1.23 | 0.22 | 0.16 | 0.83 | 0.7 | n.d. | n.d. | n.d. | n.d. |
| Br | 19 | 18 | 7.67 | 6.1 | 6.28 | 5.09 | 3.96 | 4.03 | 1540 | 1340 |
| Ca | 16 200 | 17 000 | 8930 | 8350 | 19 600 | 21 100 | 45 900 | 43 800 | 49 100 | 44 800 |
| Cd | 1.56 | 1.55 | 0.19 | 0.21 | 0.09 | 0.06 | 0.88 | 0.85 | 1.86 | 1.59 |
| Cl | n.d. | n.d. | 686 | 475 | 2400 | 1780 | 228 | 113 | 6340 | 5458 |
| Cr | 11.2 | 10.5 | 2.37 | 2.1 | 0.31 | n.d. | 341 | 377 | 1.68 | 1.84 |
| Cu | 140 | 142 | n.d. | 11 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Dy | 0.4 | 0.29 | 0.071 | 0.066 | n.d. | 0.07 | n.d. | 0.02 | n.d. | n.d. |
| Fe | 2840 | 2688 | 584 | 550 | n.d. | 23.6 | 341 | 372 | 416 | 338 |
| K | 4580 | 4370 | 1700 | 1710 | 10 800 | 9380 | 2450 | 2860 | 25 900 | 25 300 |
| La | 2.58 | 2.47 | 0.51 | 0.57 | 0.72 | 0.65 | 0.19 | 0.19 | 2.19 | 1.97 |
| Mg | 3170 | 2790 | n.d. | 881 | 2790 | 2840 | 2310 | 2090 | 10830 | 9670 |
| Mn | 169 | 162 | 15 | 15.9 | n.d. | n.d. | 12.6 | 11.5 | 252 | 222 |
| Na | 298 | 283 | 143 | 134 | 425 | 423 | 742 | 712 | 127 | 114 |
| Rb | 3.98 | 3.35 | n.d. | 1.73 | n.d. | 1.59 | 20.2 | 17.6 | 16 | 15.4 |
| Sb | n.d. | n.d. | n.d. | n.d. | 0.24 | 0.2 | n.d. | n.d. | n.d. | n.d. |
| Sm | 0.79 | 0.87 | 0.29 | 0.26 | 0.07 | 0.09 | n.d. | 0.09 | 0.2 | 0.19 |
| Ti | 179 | 192 | 85.8 | 73.7 | n.d. | 16.4 | n.d. | n.d. | n.d. | n.d. |
| V | 17.3 | 17 | 4.32 | 4.06 | 1.14 | 0.94 | 1.04 | 0.89 | n.d. | n.d. |
| Zn | 60.5 | 53.1 | 20.7 | 18.5 | 1.47 | n.d. | 27.2 | 31.4 | 33.7 | 32.3 |

S = sample concentrations obtained by direct plant tissue irradiation; A = sample concentrations derived from ashed samples analysis; n.d. = not detected.



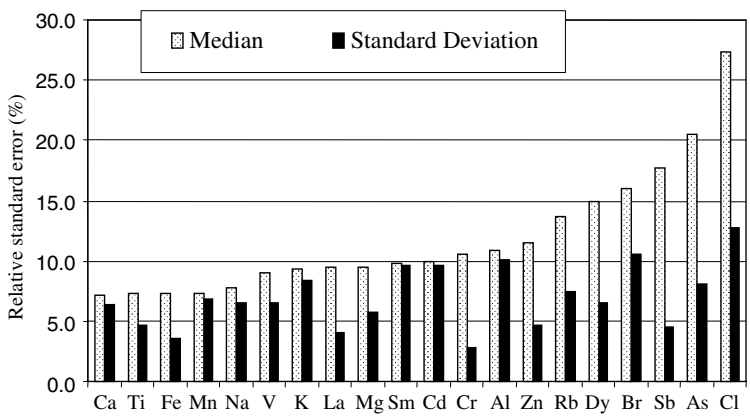


FIGURE 1 Relative standard errors of results of ashed samples analysis compared to plant tissue analysis.

(b) Elements with 10 to 15% relative standard error: these are generally elements with moderate NAA sensitivities and low sample concentrations, such as Zn, Rb, and Dy.

(c) Elements with 15 to 30% relative standard error: Br, Sb, As, and Cl. These elements are generally classified as "volatile" and the higher deviations between the results obtained for the plant and ashed samples are probably due to losses during the dry ashing. The deviations varied significantly with the plant matrix.

The categories of results not included in the plots of Fig. 1 include the following.

(i) Elements not detected in plants, but detected in ashed samples: this was observed in plants of low ash contents (e.g. banana, mango, yam, and rice) in which the high mass-reduction factors increase the element concentrations in the ashed samples. Examples are the cases of Cd (in banana), Cr (callaloo), Cu (rice, mango, yam). Where element concentrations are only just below the detection limits in plants, dry ashing may also improve the detection limit in high ash content plants (e.g. Cr in callaloo, Fe and Ti in *Tillandsia* sp.).

(ii) Elements detected in plants but not detected in ashed samples: this was observed only in the cases of Cd (in callaloo), Cr (banana, *Tillandsia* sp.), and Zn (*Tillandsia* sp.). In these cases, element concentrations were above the detection limits for the plant samples, and concentration by ashing did not achieve the levels required for the NAA detection limits for ash.

There is an interplay of factors, which include the natural concentration in the plant tissue, the mass-reduction factor, and potentially the increased detection limit in the ash matrix. For a given element, the NAA detection limits in the ash matrices are usually higher than in biological matrices [16,17]. The exact values of the detection limits in the plant and its ash may differ significantly from plant to plant, depending on the particular mineral content. This may diminish the preconcentration advantage of ashing to give a situation such as that described in (ii) above.



Although ashed sample analysis significantly extends the detection limits of the analysis to levels that are lower than would have been attained by direct sample tissue analysis, the detection limits obtained are still generally poorer than may be attained with the use of some other elemental analysis techniques, e.g. atomic absorption spectrophotometry. Thus, some common element that would have been easily detectable by atomic absorption spectrophotometry remained undetected even with the ashing preconcentration NAA. Examples (Tables IV and V) include Ca (in banana, rice, yam), Cu (callaloo, carrot, *Tillandsia*, tree bark, tomato leaves), Cr (rice, mango, yam), Fe (rice), Mn (*Tillandsia*), V (tomato leaves), and As (tree bark, tomato leaves). However, the analytical precision obtained for various elements through the ashed sample analysis (predominantly 1 to 12 %; Table III) compare well to those that would be expected through atomic absorption analysis at the prevailing element concentrations.

As illustrated in Fig. 2, using the data from Tables IV and V, the overall agreement between results obtained from both procedures is good. The coefficient of correlation obtained for 151 paired element determinations is $r^2 = 0.9978$, and the paired $t$-test indicates that there is no statistically significant difference between both NAA methods ($P = 0.801$). Furthermore, the ash analysis results for SRM 1573a tomato leaves in the last column of Table V compare well with the certified reference values given in Table I.

## CONCLUSIONS

Preconcentration of food and plant samples by dry ashing at 450°C allows the reliable determination of many elements that may be below the NAA detection limits for plant tissues using low-flux reactors. However, because of the elevated background counts of

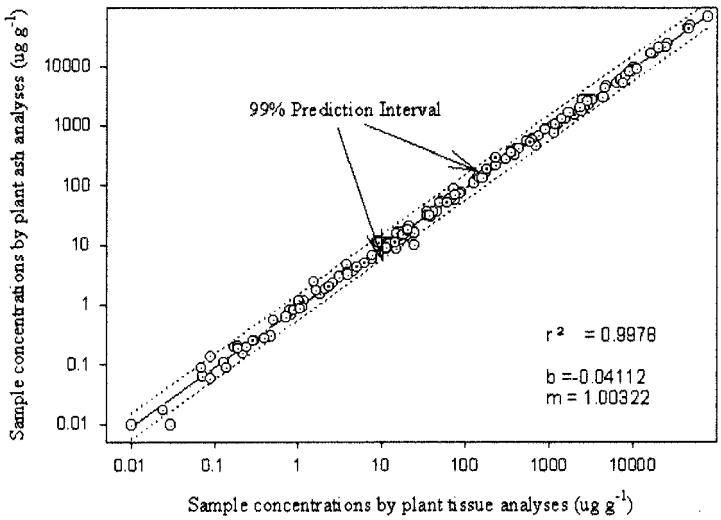


FIGURE 2 Relationship between concentrations of elements found in dry and ashed samples of plant materials.



the ash matrixes, resulting generally in higher detection limits, improved detection may not always be achieved particularly in plants with high mineral–ash contents when analyte element concentrations are low.

## *Acknowledgement*

The Third World Academy of Sciences provided a research fellowship (to P.C. Onianwa). The support of Charles Grant and Alexis Gayle in sample analysis is also acknowledged.

## *References*

[1] G. Sattarov, I.I. Orestova and A.A. Kist, *Zh. Anal. Khim.*, **38**, 1215–1218 (1983).
[2] N. Nonaka, H. Higuchi, H. Hamaguchi and K. Tomura, *Bunseki Kagaku*, **34**, 360–364 (1985).
[3] R.C. Diaz, *Alimentaria* (*Madrid*), **29**, 29–31 (1992).
[4] J. Kucera and L.J. Soukal, *Radioanal. Nucl. Chem.*, **193**, 33–38 (1995).
[5] P. Mader, V. Haber and J. Zelinka, *Analusis*, **25**, 175–183 (1997).
[6] P. Mader, J. Szakova and D. Miholova, *Analusis*, **26**, 121–129 (1998).
[7] F.M.G. Tack, S.P. Singh and M.G. Verloo, *Agrochimica*, **41**, 182–185 (1997).
[8] R. Pietra, L. Ubertalli, P. Manaktala and E. Sabbioni, *Comm. Eur. Communities* [*Rep.*] *Eur*, **9211**, 28 pp. (1994).
[9] N. Momoshima, N. Inoue and Y. Takashima, *J. Radioanal. Nucl. Chem.*, **155**, 335–342 (1991).
[10] A. Ihsanullah, *J. Radioanal. Nucl. Chem.*, **176**, 303–313 (1993).
[11] X. Hou, X. Feng, Q. Qian, C. Chai and X. Hou, *Analyst*, **123**, 2209–2213 (1998).
[12] S. Kohl, Y. Katayama, Y. Kawabata, A. Kagawa, K. Kishida, K. Nishida, T. Aoki and J. Takada, *Kyoto Daigaku Genshiro Jikkensho Gakujutsu Koenkai Hobunshu*, **32**, 77–80 (1998).
[13] L. Brighigna, M. Ravanelli, A. Minelli and L. Ercoli, *Sci. Total Environ.*, **198**, 175 (1997).
[14] P. Bohm, H. Wolterbeek, T. Verbug and L. Musilek, *Environ. Pollut.*, **102**, 243 (1998).
[15] C. Branquinho, F. Catarino, D.H. Brown, M.J. Pereira and A. Soares, *Sci. Total Environ.*, **232**, 67 (1999).
[16] C. Grant, G.C. Lalor, J. Preston, R. Rattray and M. Vutchkov, *Jam. J. Sc. Tech.*, **9**, 63 (1999).
[17] G.C. Lalor, M.K. Vutchkov, C. Grant, J. Preston, M.G. Figueiredo and D.I.T. Favaro, *J. Radioanal. Nucl. Chem.*, **244**, 263–266 (2000).