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ACID LEACHING OF VEGETABLE SAMPLES FOR MINERAL ELEMENTS ANALYSIS BY ATOMIC ABSORPTION SPECTROSCOPY

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Abstract: **Eleven vegetable samples cultivated in Nigeria were analysed for their phosphorus contents. The results indicated that the samples are rich in phosphorus. The sample with the highest phosphorus content was treated with varying concentrations of HCl, HNO_3, and H_2SO_4 acids to determine 11 mineral elements by atomic absorption spectroscopy. Analysis of the leachates found that HCl leached out pigments, which affected the absorbance behavior of several elements while with H_2SO_4, the results were lower than expected because of the formation of insoluble compounds with some elements. HNO_3 gave the best results. Leaching with 3 M HNO_3 for 1 hr gave reproducible results and accurate recoveries of spiked samples. In the reproducibility studies, coefficients of variation were 0.40% magnesium, 2.34% manganese, 2.58% calcium, 2.63% zinc, and 16.67% copper at the concentration levels obtained in that sample. Average recoveries were 97.60 ± 1.40% zinc, 99.17 ± 1.26% calcium, and 102.52 ± 7.97% magnesium. A procedure is proposed for the preparation of vegetable samples for mineral elements analysis by atomic absorption spectroscopy in the air-acetylene flame. While this method can be successfully carried out in 1 hr using an ordinary beaker, ashing requires about 3 hr to accomplish in addition to the use of a muffle furnace and a constant supply of electricity for that duration. The relative abundance of the elements in vegetables is in the order Ca>Mg>Mn>Zn>Cu>Co=Pb.**

Key Words: **Sample preparation; ashing; acid leaching; element distribution.**

INTRODUCTION

Chemical analysis has often been carried out in steps which can be broadly classified as sample preparation and analysis. Goldberg and Sacks (1982) singled out sample preparation as the factor limiting analysis time and cost. Also, according to Udoh (1989), the reliability of a set of analytical results depends on the method by which the sample is prepared for measurement. Plant samples for atomic absorption spectrometric analysis have hitherto been prepared by dry ashing and wet ashing (AOAC, 1984) and decomposition with acids or acid mixtures (Allen et al., 1974). Ashing takes about 3 hours at 500°C (the most commonly used ashing temperature) and in some cases produce a product which can become a problem in the measurement step. Some elements present in the sample become converted into forms which pose serious problems in the flame. Phosphorus, for instance, is converted into $P_2O_7^{2-}$, a very thermally stable substance which interferes with the absorption behavior of calcium in the flame. Acid mixtures

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incorporating perchloric acid are liable to explosion if dryness ensures. Although over 30 yr ago, leaching and solvent extraction procedures have been described, these have not been properly developed and applied to analysis of plant materials for metals.

The aim of this work is to produce a cheaper and easier method of sample preparation for the determination of acid-leachable mineral elements in vegetables. It examines the use of HCl, HNO_3 and H_2SO_4 acid solutions to leach out metal ions from vegetable samples for flame atomic absorption spectrometric analysis. The outcome is used to study the abundance of mineral elements in vegetables.

EXPERIMENTAL

Apparatus

1. A Unicam ultraviolet spectrophotometer equipped with a recorder and a computer.
2. A Unicam 919 atomic absorption spectrophotometer which was operated on the air-acetylene mode.
3. A Gallenkamp muffle furnace with a temperature range 0–1200°C.

Reagents

All reagents were of analytical reagent grade. Distilled water was used in all preparations and dilutions. Stock strontium solution (50,000 ppm) was prepared by dissolving 152.156 g $SrCl_2 \cdot 6H_2O$ in water and diluting it to 1 dm^3 in a volumetric flask. Hydrochloric acid solution (6 M) was prepared by diluting 518.0 cm^3 concentrated HCl (s.g.1.18, % purity 37, BDH, England) to 1 dm^3 in a volumetric flask. Stock standard solutions (1,000 ppm) of the elements were prepared as detailed in the instrument manual. Calibration solutions were prepared by serial dilutions of the stocks. Element concentrations in samples were determined by reference to the respective calibration curve. Calibration curves were prepared afresh for each subsequent analysis.

Study Samples, Samples Collection and Treatment

Vegetable plant leaves were used (Table 1). They were collected from a family orchard at Ndiya Ikot Ukap in Nsit Ubium Local Government Area of Akwa Ibom State, Nigeria. After removing the leaves from the plants, they were washed with deionized water, cut into pieces and dried in the oven (at 60°C to constant weight). The dry leaves were then blended into fine powder with an electric blender and stored for further use.

Determination of Phosphorus by the uv-vis Method

Triplicate weighing of 1.0 g of each sample powder were placed into crucibles. They were then put in a muffle furnace and ashed at 600°C. The ash was treated with 20.0 cm^3 6 M HCl solution and the resulting solution concentrated on a steam bath to ~5.0 cm^3. This solution was transferred quantitatively to a 50-cm^3 volumetric flask and diluted to the mark with water. The resulting solutions were used for the determination of phosphorus by the yellow method (Kitson and Mellon, 1944) using the ultraviolet spectrophotometer. An aliquot of the sample was pipetted using this method into a 100-cm^3 volumetric flask and 20.0 cm^3 of vanadomolybdate reagent was added and the solution diluted to the mark. (The vanadomolybdate reagent was prepared thus: 20.0 g ammonium molybdate was dissolved in 200.0 cm^3 hot water and then cooled, then 1.0 g ammonium metavanadate was also

Table 5. Effect of leaching time on mineral element levels using sample 1.

Leaching Time, hr	Levels of Elements, mg $kg^{-1} \times 10^2$ Leaf Powder					
	Ca	Mg	Zn	Mn	Cu	Co, Pb
0.5	273.08 ± 4.80	313.23 ± 0.12	0.81 ± 0.07	5.42 ± 0.04	0.17 ± 0.02	N.D.
1.0	295.00 ± 2.16	320.50 ± 3.60	1.22 ± 0.02	5.40 ± 0.00	0.28 ± 0.02	N.D.
2.0	297.50 ± 2.10	326.05 ± 3.29	1.15 ± 0.03	5.20 ± 0.00	0.29 ± 0.03	N.D.
3.0	298.00 ± 2.06	324.18 ± 6.84	1.07 ± 0.02	5.30 ± 0.00	0.29 ± 0.03	N.D.

20 mg calcium and magnesium and 25 mg zinc respectively, were added to each beaker with sample. Water (5.0 cm^3) and 15.0 cm^3 10 M HNO_3 solution were added. The mixtures were left to leach for 1 hr, filtered, washed, and the filtrate and washings transferred into 50-cm^3 volumetric flasks. In each case, 3.0 cm^3 strontium solution was added and the volume made to the mark with water. The solutions were analysed against a blank for the elements of interest (Table 7).

Sample 1, in another series of experiments, was ashed in triplicate at 600°C. The ash was dissolved in 20.0 cm^3 6 M HCl solution. This solution was concentrated on a steam bath to about 5.0 cm^3. Each solution was transferred quantitatively to a 50-cm^3 volumetric flask. Strontium solution (3.0 cm^3) was added and the solution made to the mark with water. A blank solution was also prepared. The solutions were analysed for the elements of interest and averaged (Table 8).

Analysis of Samples

Triplicate weighings of 0.50 g of each sample (other than samples 1 and 2 used in the above stages) were placed into small, clean, dry beakers. These were then processed and analyzed as described under the proposed procedure and the results averaged (Table 9).

Proposed Procedure

A known mass (0.50 g) of the sample is weighed into a 50-cm^3 beaker, 5.0 cm^3 water and 15.0 cm^3 10 M HNO_3 solution are added. The mixture is left to stand for 1 hr with occasional swirling. It is then filtered with suction. The residue is washed with aliquots of water. The combined filtrate and washings is transferred quantitatively into a 50-cm^3 volumetric flask. A strontium solution (3.0 cm^3 50,000 ppm) is added and the solution made to the mark with water. A blank solution is also prepared. All the solutions are analysed for the elements of interest with an atomic absorption spectrophotometer.

Table 6. Reproducibility of leaching with 3 M HNO_3 solution for 1 hr using sample 2.

Element	Level Obtained, mg $kg^{-1} \times 10^2$
Ca	132.30 ± 3.42
Mg	627.56 ± 2.50
Zn	1.14 ± 0.03
Mn	1.28 ± 0.03
Cu	0.36 ± 0.06
Co	N.D.
Pb	N.D.

Table 1. Names and phosphorus content of vegetable samples.

Sample Number	Sample Name	Phosphorus Content, mg $kg^{-1} \times 10^2$ Leaf Powder
1	*Assystacia gangitica*	85.83 ± 1.18
2	*Telfaria occidentalis*	85.00 ± 2.36
3	*Ocimum basilocum*	83.89 ± 0.96
4	*Amaranthus hybridus*	78.89 ± 6.94
5	*Ipomoea batatas*	54.44 ± 6.31
6	*Vernonia amygdalina*	46.00 ± 1.41
7	*Piper guineense*	42.00 ± 1.00
8	*Marsdenia latifilum*	40.00 ± 2.36
9	*Heinsia crinata*	39.17 ± 5.89
10	*Lasianthera africanum*	36.67 ± 0.00
11	*Gnetum africanum*	27.00 ± 0.00

dissolved separately in 120.0 cm^3 hot water, cooled, and 140.0 cm^3 concentrated nitric acid was added to it in a 1 dm^3 volumetric flask. The molybdate solution was gradually added to the vanadate solution and the solution diluted to the 1 dm^3 mark with water). Phosphorus standard solutions (0–5 ppm) for the preparation of the calibration curve were prepared in 100-cm^3 volumetric flasks each containing 20.0 cm^3 vanadomolybdate reagent. The absorbance of the yellow solutions was read at 400 nm. Results were averaged (Table 1).

Effect of Variation in HCl, HNO_3 and H_2SO_4 Acids Concentration on the Levels of Elements Leached Out During 0.5 hr Using Sample 1

Triplicate weighings of 0.5 g of sample 1 powder were placed into small beakers. Aliquots of each acid necessary to give the stated concentrations in 50.0 cm^3 of solution (see Tables 2–4) were transferred into the beakers. The volume of the leaching solution, in all cases, during leaching, was kept at 20.0 cm^3. The mixture was left to stand for 0.5 hr with occasional swirling. Each mixture was filtered on filter paper under suction at the expiration of 0.5 hr. The residue was washed with small volumes of water and discarded. The combined filtrate and washings was transferred quantitatively to a 50-cm^3 volumetric flask. Strontium solution (3.0 cm^3) (Udoh, 1999) was added and the solution made to the mark with water. A blank solution was prepared for each concentration of acid. These solutions were analysed for elements (Tables 2–4).

Table 2. Levels of mineral elements in leachates with HCl acid solutions in 0.5 hr using sample 1.

Molarity of Acid	Levels of Elements, mg $kg^{-1} \times 10^2$ Leaf Powder					
	Ca	Mg	Zn	Mn	Cu	Co, Pb
0	364.61 ± 15.00	126.57 ± 0.05	0.06 ± 0.00	0.14 ± 0.00	0.11 ± 0.00	N.D.
0.3	364.62 ± 11.96	470.72 ± 0.04	0.88 ± 0.00	5.57 ± 0.00	0.17 ± 0.00	N.D.
0.6	412.76 ± 9.48	382.66 ± 7.62	0.91 ± 0.00	5.85 ± 0.20	0.17 ± 0.00	N.D.
0.9	395.12 ± 8.20	365.21 ± 4.50	0.94 ± 0.02	5.52 ± 0.07	0.17 ± 0.00	N.D.
1.5	369.04 ± 6.77	357.36 ± 6.50	0.91 ± 0.20	5.38 ± 0.13	0.17 ± 0.00	N.D.
2.0	351.92 ± 4.67	347.74 ± 4.03	0.90 ± 0.15	5.15 ± 0.08	0.17 ± 0.00	N.D.
2.5	349.04 ± 8.50	347.10 ± 5.11	0.89 ± 0.06	5.19 ± 0.13	0.16 ± 0.00	N.D.
3.0	342.46 ± 10.20	330.28 ± 4.76	0.86 ± 0.05	5.23 ± 0.42	0.17 ± 0.00	N.D.

Table 3. Levels of mineral elements in leachates with HNO_3 acid solutions in 0.5 hr using sample 1.

Molarity of Acid	Levels of Elements, mg $kg^{-1} \times 10^2$ Leaf Powder					
	Ca	Mg	Zn	Mn	Cu	Co, Pb
0	364.61 ± 15.00	126.57 ± 0.05	0.06 ± 0.00	0.14 ± 0.00	0.11 ± 0.00	N.D.
0.3	329.74 ± 10.02	300.72 ± 6.28	0.86 ± 0.19	6.28 ± 0.00	0.17 ± 0.00	N.D
0.6	321.53 ± 10.30	300.82 ± 0.06	0.89 ± 0.04	6.14 ± 0.00	0.17 ± 0.00	N.D.
0.9	316.15 ± 8.50	300.99 ± 0.02	0.87 ± 0.03	5.61 ± 0.00	0.17 ± 0.00	N.D.
2.0	280.09 ± 10.20	301.09 ± 5.60	0.90 ± 0.10	5.57 ± 0.20	0.17 ± 0.00	N.D.
2.5	272.50 ± 6.50	306.97 ± 0.07	0.82 ± 0.08	5.52 ± 0.22	0.17 ± 0.00	N.D.
3.0	273.08 ± 4.80	313.23 ± 0.12	0.81 ± 0.07	5.42 ± 0.40	0.17 ± 0.00	N.D.

Effect of Leaching Time on the Levels of Elements Obtained with 3 M HNO_3 Solution Using Sample 1

Triplicate weighings of 0.5 g of sample 1 powder were placed into clean, dry beakers for each time interval considered (Table 5). A 15.0 cm^3 10 M HNO_3 solution was added to each followed by 5.0 cm^3 water. The samples were filtered and the filtrate and washings transferred into 50-cm^3 volumetric flasks at the end of 1, 2, and 3 hr intervals. Strontium solution (3.0 cm^3) was added and the solution diluted to the mark with water. A blank solution was also prepared. The solutions were analysed for the elements of interest and averaged (Tables 4–5).

Reproducibility Studies with 3 M HNO_3 Solution and Leaching Time of 1 hr

Six replicate weighings of 0.5 g of sample 2 were placed into clean dry beakers. Nitric acid solution (15.0 cm^3 10 M) was added along with 5.0 cm^3 water. The experiments were left to stand for 1 hr. The mixture was filtered under suction. The residue was rinsed free of acid and each solution transferred quantitatively into a 50-cm^3 volumetric flask. Strontium solution (3.0 cm^3) was added and the solution made to the mark with water. A blank solution was also prepared. The solutions were analysed for the elements of interest and averaged (Table 6).

Test of Accuracy and Efficiency of Leaching

Triplicate weighings of 0.5 g of sample 2 were placed into small, clean dry beakers. Calculated amounts of $CaCO_3$ (0.050 g), MgO (0.033 g) and ZnO (0.031 g) containing

Table 4. Levels of mineral elements in leachates with H_2SO_4 acid solutions in 0.5 hr sample 1.

Molarity of Acid	Levels of Elements, mg $kg^{-1} \times 10^2$ Leaf Powder					
	Ca	Mg	Zn	Mn	Cu	Co, Pb
0	364.61 ± 15.00	126.57 ± 0.05	0.06 ± 0.00	0.14 ± 0.00	0.11 ± 0.00	N.D.
0.3	158.65 ± 6.79	113.18 ± 0.50	0.76 ± 0.06	4.90 ± 0.50	0.17 ± 0.00	N.D.
0.6	144.23 ± 13.59	113.16 ± 0.85	0.81 ± 0.01	4.87 ± 0.00	0.17 ± 0.00	N.D.
0.9	133.01 ± 13.88	110.42 ± 0.35	0.87 ± 0.15	4.95 ± 0.02	0.17 ± 0.00	N.D.
1.5	128.21 ± 7.34	80.13 ± 0.08	0.95 ± 0.06	4.89 ± 0.01	0.17 ± 0.00	N.D.
2.0	128.21 ± 7.71	80.12 ± 0.08	0.79 ± 0.11	4.77 ± 0.03	0.17 ± 0.00	N.D.
2.5	115.39 ± 10.40	65.92 ± 0.02	0.81 ± 0.17	4.93 ± 0.04	0.17 ± 0.00	N.D.
3.0	91.34 ± 10.10	61.18 ± 0.03	0.78 ± 0.07	5.00 ± 0.01	0.17 ± 0.00	N.D.

Table 5. Effect of leaching time on mineral element levels using sample 1.

Leaching Time, hr	Levels of Elements, mg $kg^{-1} \times 10^2$ Leaf Powder					
	Ca	Mg	Zn	Mn	Cu	Co, Pb
0.5	273.08 ± 4.80	313.23 ± 0.12	0.81 ± 0.07	5.42 ± 0.04	0.17 ± 0.02	N.D.
1.0	295.00 ± 2.16	320.50 ± 3.60	1.22 ± 0.02	5.40 ± 0.00	0.28 ± 0.02	N.D.
2.0	297.50 ± 2.10	326.05 ± 3.29	1.15 ± 0.03	5.20 ± 0.00	0.29 ± 0.03	N.D.
3.0	298.00 ± 2.06	324.18 ± 6.84	1.07 ± 0.02	5.30 ± 0.00	0.29 ± 0.03	N.D.

20 mg calcium and magnesium and 25 mg zinc respectively, were added to each beaker with sample. Water (5.0 cm^3) and 15.0 cm^3 10 M HNO_3 solution were added. The mixtures were left to leach for 1 hr, filtered, washed, and the filtrate and washings transferred into 50-cm^3 volumetric flasks. In each case, 3.0 cm^3 strontium solution was added and the volume made to the mark with water. The solutions were analysed against a blank for the elements of interest (Table 7).

Sample 1, in another series of experiments, was ashed in triplicate at 600°C. The ash was dissolved in 20.0 cm^3 6 M HCl solution. This solution was concentrated on a steam bath to about 5.0 cm^3. Each solution was transferred quantitatively to a 50-cm^3 volumetric flask. Strontium solution (3.0 cm^3) was added and the solution made to the mark with water. A blank solution was also prepared. The solutions were analysed for the elements of interest and averaged (Table 8).

Analysis of Samples

Triplicate weighings of 0.50 g of each sample (other than samples 1 and 2 used in the above stages) were placed into small, clean, dry beakers. These were then processed and analyzed as described under the proposed procedure and the results averaged (Table 9).

Proposed Procedure

A known mass (0.50 g) of the sample is weighed into a 50-cm^3 beaker, 5.0 cm^3 water and 15.0 cm^3 10 M HNO_3 solution are added. The mixture is left to stand for 1 hr with occasional swirling. It is then filtered with suction. The residue is washed with aliquots of water. The combined filtrate and washings is transferred quantitatively into a 50-cm^3 volumetric flask. A strontium solution (3.0 cm^3 50,000 ppm) is added and the solution made to the mark with water. A blank solution is also prepared. All the solutions are analysed for the elements of interest with an atomic absorption spectrophotometer.

Table 6. Reproducibility of leaching with 3 M HNO_3 solution for 1 hr using sample 2.

Element	Level Obtained, mg $kg^{-1} \times 10^2$
Ca	132.30 ± 3.42
Mg	627.56 ± 2.50
Zn	1.14 ± 0.03
Mn	1.28 ± 0.03
Cu	0.36 ± 0.06
Co	N.D.
Pb	N.D.

Table 7. Recovery studies data using sample 2.

Element	Concentration, mg		Average	S.D.	% Recovery
	Added	Recovered			
Ca	20.00	20.10			
	20.00	19.80			
	20.00	19.60	19.83	0.25	99.17 ± 1.26
Mg	20.00	19.90			
	20.00	19.30			
	20.00	22.31	20.50	1.59	102.52 ± 7.97
Zn	25.00	24.50			
	25.00	24.00			
	25.00	24.70	24.40	0.36	97.60 ± 1.40

RESULTS AND DISCUSSION

Phosphorus Determination

The phosphorus content of the vegetable samples compare well with those obtained by Udoh (1999) for similar samples obtained from a different locality (Table 1). Variations could be attributed to weather, soil condition, or fertilizer application among other factors. Phosphorus interferes in the absorption behavior of calcium in the air acetylene flame. The degree of interference should be maximum in the sample with the highest concentration of phosphorus. Sample 1 (*Assystacia gangitica*) with the highest phosphorus content was therefore selected for use in the preliminary stages of this work. Udoh (1999) had shown that incorporation of 3,000 ppm strontium in the vegetable sample solution completely eliminates the interference because of phosphorus. Since the levels of phosphorus obtained in this work are not higher than those reported for similar samples (Udoh, 1999), 3,000 ppm strontium solution was incorporated in the sample solutions for mineral elements analysis.

Preliminary Leaching Experiments with Mineral Acid Solutions

Results of mineral elements levels after leaching sample 1 with hydrochloric acid solutions for 0.5 hr are reported in Table 2. Leachates with hydrochloric acid were greenish in color. The green color changed to near black color which increased in intensity as the concentration of the acid increased. It appears from the results that hydrochloric acid leached out the plant pigments causing a positive interference on the absorption behavior of the elements to the extent that values obtained were unnecessarily higher. However,

Table 8. Comparison of methods using sample 1.

Element	Level Obtained, mg $kg^{-1} \times 10^2$ Leaf Powder	
	Leaching*	Ashing
Ca	296.83 ± 1.61	296.79 ± 2.78
Mg	323.58 ± 2.82	356.60 ± 2.83
Zn	1.15 ± 0.08	1.11 ± 0.02
Mn	5.30 ± 0.10	5.40 ± 0.34
Cu	0.29 ± 0.01	0.27 ± 0.02
Co	N.D.	N.D.
Pb	N.D.	N.D.

* Averages of the results from Table 5.

Table 9. Levels of mineral elements in vegetable samples.

Sample Number	Levels of Elements, mg $kg^{-1} \times 10^2$ Leaf Powder					
	Ca	Mg	Zn	Mn	Cu	Co,Pb
1	296.83 ± 1.61	352.24 ± 3.52	1.14 ± 0.08	5.42 ± 0.42	0.29 ± 0.01	N.D.
2	132.30 ± 3.42	627.56 ± 2.50	1.14 ± 0.03	1.28 ± 0.03	0.36 ± 0.06	N.D.
3	411.25 ± 3.61	140.51 ± 9.96	1.07 ± 0.03	0.40 ± 0.02	0.51 ± 0.00	N.D.
4	623.75 ± 3.01	399.93 ± 10.78	0.99 ± 0.02	0.35 ± 0.02	0.19 ± 0.02	N.D.
5	202.92 ± 6.25	140.51 ± 0.00	0.55 ± 0.01	0.44 ± 0.00	0.19 ± 0.03	N.D.
6	273.75 ± 7.22	166.39 ± 2.85	1.00 ± 0.06	1.64 ± 0.04	0.31 ± 0.02	N.D.
7	594.59 ± 9.54	227.56 ± 8.15	1.06 ± 0.01	3.83 ± 0.05	0.26 ± 0.00	N.D.
8	369.59 ± 3.61	436.96 ± 2.99	0.97 ± 0.02	27.09 ± 0.00	0.26 ± 0.00	N.D.
9	293.54 ± 2.21	201.68 ± 5.00	0.70 ± 0.03	3.60 ± 0.06	0.11 ± 0.00	N.D.
10	340.42 ± 6.25	248.74 ± 7.42	0.89 ± 0.01	5.53 ± 0.00	0.18 ± 0.02	N.D.
11	199.80 ± 4.42	112.27 ± 0.00	0.35 ± 0.01	2.73 ± 0.02	0.13 ± 0.02	N.D.

these values decreased as the concentration of the acid in the leaching mixture increased. This again presupposes that as the concentration of the acid increased, the leached pigment gets decomposed by the acid to form carbon which made the solutions appear black and whose particles settled on standing. However, the external effect of leaf pigments on the absorbance behavior of metal ions in the air-acetylene flame has not been investigated.

Leachates produced with nitric acid were light yellow to orange in color probably because nitric acid when exposed to decomposition conditions produces nitrogen dioxide which usually imparts a characteristic yellow color to exposed nitric acid. The results (Table 3) indicated that there was a slight decrease in the levels of the elements with increase in acid concentration, but the extent of decrease was negligible with higher acid concentration. The color of the leachates with nitric acid and the results obtained for the different elements made nitric acid the most preferable to use. Dilute nitric acid is a solvent for most metals (Brown, 1967) and most nitrates are soluble in water (Cotton and Wilkinson, 1988).

The levels of the mineral elements when the sample was leached with sulfuric acid solutions are presented in Table 4. Concentrated sulfuric acid is a dehydrating agent. Leachates with this acid had blackish (or brown) color, the intensity of which increased as the concentration of the acid increased. Sulfuric acid solutions are generally not preferred as solvents for dissolving even ash or other samples for mineral elements analysis. This is because most sulfates (e.g., $CaSO_4$ and $MgSO_4$) are insoluble in water or reaction of sulfuric acid with most metals forms an insoluble coating which protects the metal from further attack and hence cannot give accurate results of mineral analysis. The levels of mineral elements obtained in leachates using sulfuric acid (Table 4) were generally low and poorer especially for calcium and magnesium than those obtained with hydrochloric and nitric acid solutions. The low results also decreased with increasing acid concentration. In an application of the Institute of Petroleum (1985) method for the determination of metal ions in crude oil and in which 5 N sulfuric acid solution is used to dissolve the ash, Udoh (1989) observed that the results were poorer than those obtained when HCl solution was used.

Effect of Variation in Leaching Time with HNO_3 Acid on the Levels of Mineral Elements Obtained Using Sample 1

The results (Table 5) indicate that the levels of mineral elements obtained after 1 hr of leaching were similar to those obtained after 3 hr of leaching. Thus, at least a leaching time

of 1 hr is necessary for optimum results. Samples were therefore leached for 1 hr before filtration was effected.

Reproducibility of Leaching with 3 M HNO_3 for 1 hr Using Sample 2

Leaching vegetable leaf samples with 3 M nitric acid for mineral elements determination gives highly reproducible results (Table 6). The coefficients of variation were: 2.58% calcium, 0.40% magnesium, 2.63% zinc, 2.34% manganese, and 16.67% copper.

Accuracy and Efficiency of Leaching with 3 M HNO_3 for 1 hr Using Sample 2

Calcium recovery was 99.17 ± 1.26%, magnesium 102.52 ± 7.97%, and zinc 97.60 ± 1.40% (Table 7). Application of the *t*-test at 95% confidence level to replicate recovery values showed no significant differences between the amount added and the amount observed indicating quantitative recovery. Variations in the recovery values could be attributed to current fluctuations and variations in instrument response during analysis.

The proposed leaching procedure results are similar to those obtained when the sample powder was ashed and the solubilized ash solution analysed (Table 8). Hence, the proposed procedure is a good substitute for ashing which requires electricity supply of the correct voltage for at least 3 hr and a special instrument, the muffle furnace, which may not be available in most third world laboratories.

Relative Abundance of the Elements

The mineral element content of vegetables may be affected by plant species, weather, fertilizer application, extent of environmental pollution and other soil conditions: pH, soil cation exchange capacity and binding to different soil components (Kabata-Pendias and Pendias, 1984). The levels of the mineral elements obtained with each sample reveal that the most abundant element is calcium followed by magnesium, manganese, zinc and copper, in that order (Table 9). This observation is similar to what Udoh (1999) made for similar vegetable samples. Lead, chromium and cobalt were not detected in any of the vegetable samples. Lead is mainly absorbed through plant leaves after aerial deposition (Allegria et al., 1991). Adsorption through the root is negligible (Allegria et al., 1991). Washing of the leaves removes up to 50% of the lead that settles on them. Thoroughly rinsing with water removes dust particles which usually contain traces of lead and hinders the presence of lead in vegetables. Variations in the levels of metals obtained in this work and those obtained in previous works could be attributed to factors already mentioned. Vegetables can serve as a rich source of essential mineral elements like calcium, magnesium, and zinc. The environment where the vegetables are grown is relatively free from contamination by heavy metals (Table 9).

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