

## Levels of Some Major and Trace Elements in Commercial Mango Fruit Juices determined by Flame Atomic Absorption Spectrometry

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**Summary:** A simple and low cost method has been described for the determination of Na, K, Ca, Cr, Fe and Zn in mango fruit juices using atomic absorption spectrometry. The method involves digestion of samples with nitric acid at 105°C on an oil bath for 45 minutes. Relative standard deviation for major elements was better than 1% and for trace elements around 7%. The concentration ranges for Na, K, Ca, Cr, Fe and Zn are 81-300, 49-570, 36-181, 0.075-0.250, 0.80-2.03 and 0.05-0.70 µg/g respectively.

### Introduction

In the development of an analytical method many considerations are to be taken into account. They may include reduction in time and cost of methods of analysis, use of resources, production of waste products and also possible reduction in energy consumption. Above all the accuracy and precision of a method is desired.

Elemental analysis (including trace elements) of food materials is very important for the assessment of nutrients and environmental effects on humans. The environmental term includes origin of food, i.e., animal or plant, the soil on which food or its ingredients are grown, food processing and preservation and nature of food i.e., fresh, frozen, cooked semicooked, solid or liquid.

In metal elemental analysis of biological materials and food stuffs the digestion is the very basic step. Classical wet digestion methods are generally employed. They give complete destruction of organic matter and bring the desired elements into solution. These procedures take a long time to complete.

Atomic absorption spectrometric methods require complete dissolution of elements rather than complete digestion of the sample. This criterion may lead to reduction in heating time required for this purpose.

A variety of decomposition methods using mineral acids in open and closed systems are

reported [1,2]. Wet digestion methods are generally preferred over dry ones. It is believed that the total acid digestion of biological and food materials can bring all the desired elements into solution. For this purpose single acid or mixture of acids with or without oxidizing agents is required.

Nitric acid [3,4] alone or in combination with hydrogen peroxide [5,6], HF-HClO<sub>4</sub> [7], perchloric acid [5-8], sulphuric acid and H<sub>2</sub>SO<sub>4</sub>-HClO<sub>4</sub> [8] and H<sub>2</sub>O<sub>2</sub>-HF [9] have been suggested for wet digestion of various food stuffs of plant and animal origin. Furthermore hydrochloric acid, HCl-H<sub>2</sub>O<sub>2</sub> [3] and H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O<sub>2</sub> [5] are also reported for this purpose with certain limitations.

Every decomposition method may be excellent within its specific experimental conditions and materials studied. For routine elemental analysis of food materials simple digestion method is required which should bring the desired elements into solution efficiently in a single digestion step using average laboratory facilities. It should have easy handling efficient short digestion time and low consumption of minimum number of reagents.

The idea underlying the partial digestion is to bring the desired elements into solution as compared to total digestion method using H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O<sub>2</sub> [10,11]. Successful use of partial digestion with nitric acid for biological tissues [12] and food stuff [13] have already been reported. This work reports on the levels of some major and trace

elements in commercial mango fruit juices using nitric acid digestion by flame atomic absorption spectrometry (FAAS).

## Results and Discussion

### Optimization of digestion conditions

To establish the optimum amount of nitric acid required for satisfactory extraction of elements, four sets of test tube pairs each containing 10 ml of a juice sample and 2,5,8 and 10 ml of nitric acid respectively were taken and digestion was done for 30 minutes at  $105 \pm 1^\circ\text{C}$  on oil bath. Blanks were similarly prepared. After dilution and making up the volume, samples were analysed for elements using instrumental conditions given in Table-1. Preliminary results indicated that 5 ml nitric acid is sufficient to bring the maximum of test elements into solution. Further excess of acid has no significant effect on the results.

Table-1: Instrumental parameters for the determination of elements by flame atomic absorption spectrometry.

Element	Na	K	Ca	Cr	Fe	Zn
Wave Length (nm)	589.0	766.5	422.7	357.9	248.3	213.8
Slit Width(nm)	0.4	2.6	0.4	1.3	0.2	1.3
Lamp Current(mA)	10.0	10.0	7.5	7.5	10.0	10.0
Air flow rate (l/min)	9.5	9.5	9.5	9.5	9.5	9.5
Acetylene flow Rate(l/min)	2.2	2.3	2.5	2.6	2.3	2.0
Integration time(sec)	2.0	2.0	2.0	2.0	2.0	2.0
Burner Height (mm)	7.5	7.5	10.0	7.5	7.5	7.5

To optimize the heating time a set of 10 ml of a juice sample in duplicate was digested with 5 ml nitric acid for 15, 30, 45 and 60 minutes at  $105 \pm 1^\circ\text{C}$  and analysed as described above. Results showed that satisfactory extraction has been achieved in between 30-45 minutes. Thus for further work for a 10 ml juice sample containing 5 ml nitric acid a heating time of 45 minutes was followed.

### Blank values

Blank values for the elements under study were also determined for the assesment of possible contamination level in the procedure adopted. A set of five tubes each containing 5 ml nitric acid and 10 ml water was subjected through the procedure. After dilution and making up the volume to 25 ml,

concentration of sodium, potassium, calcium, chromium, iron and zinc were determined by FAAS. Concentration ranges for Na,  $2.5 \pm 2 \mu\text{g ml}^{-1}$ ; K,  $0.2 \pm 0.2 \mu\text{g ml}^{-1}$ ; Ca,  $0.3 \pm 0.2 \mu\text{g ml}^{-1}$ ; Cr,  $0.01 \pm 0.01 \mu\text{g ml}^{-1}$ , Fe  $0.15 \pm 0.03 \mu\text{g ml}^{-1}$  and Zn,  $0.03 \pm 0.01 \mu\text{g ml}^{-1}$  were obtained. These blank values are low and do not cause any problem in the determination of elements.

### Accuracy and Control

Accuracy for the proposed method was determined by standard addition method. For this purpose a juice sample in duplicate with and without addition of known amounts chromium, iron and zinc was digested as described and analysed. Sample blanks were also prepared. The results are given in Table-2. They indicate that %age recovery of these elements is satisfactory. Precision for n determinations (n=5-6) was expressed in relative standard deviation (RSD). For elements found in higher concentration i.e., Na, K and Ca precision obtained at several occasion was better than 1%. Precision for Cr, Fe and Zn present at lower concentration level was around 7%, which is quite acceptable. Results obtained by proposed method are given Table-3. Each value is a mean of at least 3 independent batches prepared in duplicate and each sample analysed at least twice for each element.

Table-2: Recovery of Chromium, Iron and ( $\mu\text{g ml}^{-1}$ ) in a Mango Juice Sample

Trace Element	Added	Found	% age recovery
Chromium	-	$0.175 \pm 0.010$	-
	0.100	$0.277 \pm 0.020$	102
	0.150	$0.323 \pm 0.020$	98.7
Iron	-	$1.05 \pm 0.03$	-
	1.00	$2.06 \pm 0.05$	101
	1.50	$2.54 \pm 0.05$	99.3
Zinc	-	$0.175 \pm 0.010$	-
	0.100	$0.276 \pm 0.020$	101
	0.150	$0.324 \pm 0.020$	99.3

## Experimental

### Reagents

Deionized water was used throughout. Standard stock solutions ( $1\text{g l}^{-1}$ ) were prepared by dissolving appropriate amount of Merck Anal. R grade  $\text{CaCl}_2$ ,  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{KCl}$ ,  $\text{NaCl}$

Table-3: Analytical results of some commercial mango fruit juices obtained by partial digestion with nitric acid.

Sample	Concentration ( $\mu\text{g ml}^{-1}$ )					
	Na	K	Ca	Cr	Fe	Zn
1	98.8 $\pm$ 2	570.0 $\pm$ 8	36.1 $\pm$ 0.5	0.125 $\pm$ 0.01	1.20 $\pm$ 0.01	0.050 $\pm$ 0.01
2	190.3 $\pm$ 4	93.8 $\pm$ 2	97.5 $\pm$ 1.0	0.125 $\pm$ 0.01	1.85 $\pm$ 0.02	0.325 $\pm$ 0.01
3	300.3 $\pm$ 4	57.8 $\pm$ 2	89.6 $\pm$ 0.5	0.150 $\pm$ 0.01	1.38 $\pm$ 0.02	0.700 $\pm$ 0.01
4	210.8 $\pm$ 3	126.0 $\pm$ 3	68.4 $\pm$ 0.4	0.250 $\pm$ 0.01	0.63 $\pm$ 0.01	0.100 $\pm$ 0.01
5	197.3 $\pm$ 4	320.0 $\pm$ 4	79.9 $\pm$ 0.9	0.150 $\pm$ 0.01	1.18 $\pm$ 0.02	0.125 $\pm$ 0.01
6	285.3 $\pm$ 4	48.8 $\pm$ 1	181.0 $\pm$ 1.2	0.075 $\pm$ 0.01	0.78 $\pm$ 0.01	0.300 $\pm$ 0.01
7	129.4 $\pm$ 3	270.0 $\pm$ 4	76.7 $\pm$ 1.0	1.175 $\pm$ 0.01	1.05 $\pm$ 0.03	0.175 $\pm$ 0.01
8	80.8 $\pm$ 2	240.9 $\pm$ 4	109.6 $\pm$ 1.0	0.125 $\pm$ 0.01	0.95 $\pm$ 0.01	0.150 $\pm$ 0.01
9	92.2 $\pm$ 2	245.0 $\pm$ 5	52.1 $\pm$ 0.3	0.175 $\pm$ 0.01	2.03 $\pm$ 0.03	0.150 $\pm$ 0.01
10	103.1 $\pm$ 2	225.6 $\pm$ 3	123.2 $\pm$ 1.0	0.225 $\pm$ 0.01	1.48 $\pm$ 0.02	0.275 $\pm$ 0.01
11	150.7 $\pm$ 2	260.8 $\pm$ 3	122.0 $\pm$ 2.0	0.200 $\pm$ 0.01	1.20 $\pm$ 0.04	0.200 $\pm$ 0.01

and  $\text{ZnCl}_2$  in 5% aqueous  $\text{HNO}_3$ . These solutions were diluted with 5%  $\text{HNO}_3$  to obtain working standard solutions with concentrations appropriate to FAAS measurements immediately before use. Nitric acid used in digestion and solution preparation was also Anal. R grade (65% sp.g. 1.42).

#### Sample collection

Commercial mango fruit juices of some popular brands (tetrapacks and bottles) were purchased from city markets and stored in fridge in their original packing. They were thoroughly mixed before use.

#### Contamination control

All glassware were soaked in chromic acid for 24 hours and washed with water oven dried and stored in dust and fume free atmosphere without touching their insides.

Pre-treated filter papers were used to filter digested juice samples. For this purpose they were soaked in 0.1 M (approximate) disodium salt of EDTA and washed with water to remove suspected metal impurities. The process was continued until washings were free from traces of sodium.

#### Instrumentation

A Hitachi model A-1800 Atomic Absorption Spectrophotometer equipped with standard burner and air-acetylene flame was used. Standard hollow cathode lamps were used as radiation source for sodium potassium, calcium, chromium, iron and zinc. In calculating the absorbance data, atomic

absorbance (concentration) measurement mode with integration of absorbance signals was employed. The opted instrumental conditions for each element are listed in Table-1.

A 600 ml glass beaker containing liquid paraffin was used as oil bath and a gas burner as heating source. Digestion with nitric acid was carried out in acid washed pyrex glass tubes (1.7 x 14.5 cm).

#### Digestion, sample preparation and analysis

10 ml aliquote of each juice sample in two separate acid washed glass test tubes (1.7 x 14.5 cm) was taken and 5 ml of nitric acid (sp.g. 1.42) was added into each. Tubes were heated in a pre-heated liquid paraffin bath at 105°C for forty five minutes. The test tubes were occasionally shaken manually during heating for mixing and to subside the vigorous reaction. Any floating material/suspension in digested juice samples was removed by filtration through pre-treated filter paper. Filtrate and washings were collected in 25 ml volumetric flask and made up to the mark with water. These solutions were appropriately diluted with water if required prior to direct measurement by FAAS. Blanks, standard solution, sample blanks and samples were directly aspirated and absorbance measured.

#### Conclusion

From the analytical results given in Table-3, the observed concentration range for major elements in studied juice samples is as follows:

Na. 81-300; K. 49-570 and Ca. 36-181  $\mu\text{g ml}^{-1}$

The found range of Na, K and Ca in these juice samples is generally tolerable for human consumption. In USA, the usual adult daily intake for Na is 10g of NaCl equivalent, for K 3.7-9.5 g of KCl equivalent and the usual adult daily intake of Ca in western populations is 0.4-1.3 g [14]. The British water quality control has permitted concentration values for Na, K and Ca are 150 mg, 12 mg and 60 mg per litre respectively in drinking waters [15].

The observed concentration range for trace elements in the fruit juice is as follows:

Cr, 0.075-0.250, Fe, 0.80-2.03 and Zn, 0.05-0.70  $\mu\text{g ml}^{-1}$

In USA the usual adult daily intake of Cr, Fe and Zn is 5-150  $\mu\text{g}$  10-30 mg and 6-15 mg respectively [14]. The British permitted concentration for Cr, Fe and Zn are 50, 200 and 5000  $\mu\text{g}$  respectively per litre of drinking water [15].

From the analytical results it is also clear that accuracy and precision is satisfactory. Heating time of 45 minutes is sufficient for the digestion procedure developed for the analysis of Na, K, Ca, Cr, Fe and Zn in commercial mango fruit juices. The procedure may be extended for other liquid food materials such as beverages and milk and body fluids such as urine. The method requires liquid paraffin in a glass beaker or any other container (such as cheaper aluminium ware) of suitable dimension, a heating arrangement (a gas burner or electric) and some test tubes. The number of samples in a run is determined by the dimension of liquid paraffin container used for digestion. In a 600 ml glass beaker 10 test tubes can be easily handled.

Thus it is a safe, simple and low cost sample preparation method. Further work is in process to evaluate its use for other types of samples.

#### References

1. Z. Sulcek and P. Povondra, 'Methods of Decomposition in Inorganic Analysis', CRC Press, Florida (1989).
2. J.C. Van Loon, 'Selected Methods of Trace Metal Analysis in Biological and Environmental Samples', John Wiley, New York (1985).
3. E.V. Williams, *J. Fd. Technol.*, **13**, 367 (1978).
4. H.M. Kingston and L.B. Jassie, *Anal. Chem.*, **58**, 2534 (1986).
5. A.F. Ward, L.F. Marciello, C. Carrara and V.J. Luciano, *Spectrosc. Letters*, **13**, 803 (1980).
6. A. Abu-Samara, J.R. Morris and S.R. Koirtyohann, *Anal. Chem.*, **47**(8), 1475 (1975).
7. N.R. McQuakar, D.F. Brown and P.D. Kluckner, *Anal. Chem.*, **51**, 1082 (1979).
8. Analytical Methods Committee, *Analyst*, **85**, 643 (1960).
9. E.J.M. Temminghoff and Ivo Novozamsky, *Analyst*, **117**, 23 (1992).
10. Analytical Methods Committee, *Analyst*, **92**, 403 (1967).
11. *ibid.*, **101**, 62 (1976).
12. S.B. Niazi, D. Littlejohn and D.J. Halls, *Analyst*, **118**, 821 (1993).
13. D.J. Halls, S.B. Niazi and D. Littlejohn, Poster-Colloquium Spectroscopicum Internationale, York (U.K.), July (1993).
14. S.S. Brown and Y. Kodama (ed.) 'Toxicology of Metals', clinical and experimental research", Ellis Horwood Limited, UK (1987).
15. British Water Quality Act, Sec. 20(5) (b), Department of Environments (UK) (1989).